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Analysis of Chemistry Mechanisms and Photochemical Dispersion Models for Use in Simulating Methanol Photochemistry

Radian Corp., Austin, TX

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This report reviews avaiable chemistry mechanisms and photochemical models and, recommends the most appropriate chemistry mechanism and model for assessing the photochemistry of emissions from methanol-fueled vehicles. A sensitivity analysis is also performed using the most promising chemistry mechanisms to aid in making the recommendation.

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1.0 INTRODUCTION

The Environmental Protection Agency (EPA) has contracted with Radian Corporation to perform analyses related to the use of methanol as an alternative fuel. Under this contract, Radian reviewed photochemical reaction mechanisms and atmospheric dispersion models available for use in assessing conversion of mobile sources to methanol fuel. This information is necessary for future analysis of the potential improvements in air quality from using methanol as an alternative fuel. This report summarizes the results of the analyses performed by Radian under this contract.

1.1 Background

Methanol has been proposed as an alternative fuel for motor vehicles. Because it is a chemically simpler fuel and burns much cleaner than gasoline, methanol has the potential to substantially reduce the emissions from automobiles. However, the impact of methanol-fueled vehicles on air quality needs to be investigated. Specifically, the potential impact of the methanol combustion products on ozone levels must be ascertained. The effect of methanol and methanol-associated combustion products on ozone formation will be a significant factor in the decision to encourage or discourage the use of methanol as an alternative motor vehicle fuel.

Two preliminary studies have analyzed the impacts that methanol fuel conversion may have on ozone formation in Los Angeles. In each study, emissions of ozone precursor pollutant from methanol-fueled vehicles were analyzed by using detailed photochemical dispersion models. Both studies reported that the peak ozone level would almost certainly be reduced by at least 10-20% if 100% of the on-road motor vehicles were operated on methanol. One of these studies considered only conversion of spark-fired vehicles, while the other included all vehicles.

One of these studies was performed by Whitten and Hogo of Systems Applications, Inc. (SAI) of San Rafael, California, for ARCO Petroleum Products Company, DuPont, and Standard Oil of Ohio (SOHIO). The study is entitled "Impact of Methanol on Smog: A Preliminary Estimate" (SAI, 1983). The second study was performed by the Jet Propulsion Laboratory (JPL) of the California Institute of Technology (CIT). The study was performed for the California Energy Commission and is entitled "California Methanol Assessment: Volume II: Technical Report: Chapter 6: Air Quality Impact of Methanol Use in Vehicles" (CIT, 1983).

These studies are referred to hereafter as the SAI (1983) and the CIT (1983) reports.

1.2 Objective

Because of the preliminary nature of these studies, EPA contracted with Radian to provide background information in preparation for more extensive studies. Two specific tasks were assigned to Radian.

Task 1: Review and analyze literature data concerning the effects of methanol and methanol combustion products on atmospheric chemistry. Next, select and modify for methanol chemistry those chemistry reaction mechanisms most appropriate for use in simulation of methanol photochemistry. After selection of the mechanisms, determine through a modeling sensitivity analysis the most appropriate mechanism or mechanisms to be used to simulate methanol photochemistry.

Task 2: Review existing, available dispersion models that could potentially be used to perform simulations of various methanol emission scenarios. Using the mechanism identified in Task 1, select the most appropriate model for use in simulating ozone formation.

No attempt to actually install the selected mechanism in the selected model is to be made. Also, any attempt to determine the impacts of methanol fuel conversions is beyond the scope of work of the study.

1.3 Report Description

The remainder of this report discusses in detail the results of the two tasks performed by Radian.

Section 2.0 discusses in detail the photochemistry associated with methanol and methanol combustion products. Included in the section is a discussion of emissions from methanol-fueled vehicles, the specific chemical reactions associated with methanol, and a brief review of potential mechanisms. Also included in this section is a comparison of the results obtained from the SAI and CIT modeling studies.

Section 3.0 reviews in detail the eight photochemical dispersion models that could be used to simulate methanol photochemistry in the atmosphere. The models range from relatively simplistic trajectory (Lagrangian) models to exceedingly complex numerical grid (Eulerian) models.

Section 4.0 discusses the three chemistry reaction sets selected for use in the modeling sensitivity runs and the modification of the mechanisms to handle methanol photochemistry. The implementation on the dispersion model used in the sensitivity runs is also discussed.

Section 5.0 describes the sensitivity modeling analyses performed using the three selected mechanisms.

Finally, Section 6.0 summarizes the recommendations made as to the most appropriate model and mechanisms to be used to simulate methanol photochemistry.

2.0 ANALYSIS OF AVAILABLE CHEMISTRY MECHANISMS FOR ASSESSING THE USE OF METHANOL AS A MOBILE-SOURCE COMBUSTION FUEL

At the heart of any photochemistry model is the chemistry mechanism, i.e., the set of reactions that is used to simulate actual photochemistry. The purpose of this section is to (1) review the emissions that occur from methanol-fueled vehicles, (2) review the generally recommended reactions which must be added to a photochemical smog model to account for the presence of methanol and its by-products (formaldehyde and perhaps methyl nitrite), and to (3) review the available photochemical mechanisms. A detailed discussion of each mechanism selected is given in Section 4.0.

To assess the possible impact of large-scale conversion to methanol in the Los Angeles Basin, two major studies have been carried out (SAI, 1983; CIT, 1983). Each study was done by a group with extensive background work in the area of photochemical modeling and with experience applicable to the Los Angeles region. Both studies reported that the peak ozone would almost certainly be reduced by at least 10-20% if 100% of the spark-fired motor vehicles (CIT) or all vehicles (SAI) were operated on methanol. Even greater reductions are potentially possible since each group felt that many of the assumptions used in their respective studies were conservative (i.e., tended to underpredict the possible benefits).

This section comments on the approaches, assumptions, models and range of validity of the results for the above two studies. For particularly critical points, sensitivity studies of the different chemistries will be recommended to better define their precision and accuracy. The results of these sensitivity studies are reported in Section 5.0. Suggestions for additional information or research will be made where warranted.

2.1 Methanol-Fueled Vehicle Emissions

When modeling the potential impact of gasoline replacement by methanol, changes in the emissions inventory of the mobile source fleet can be significant. This section discusses four aspects of emissions from methanol-fueled vehicles.

2.1.1 Alteration of Emissions Inventory

One of the potential advantages of using methanol as a fuel is that it burns relatively clean and evaporative emissions are simple and comparatively unreactive. Compared to gasoline, burning methanol generally results in fewer combustion products. The main combustion products are unburned methanol, formaldehyde (HCHO, a partial combustion product), CO, NO_x, and smaller amounts of post-combustion combination products, perhaps the only one of importance being methyl nitrite ($MeNO_2$). Because methanol burns cooler than gasoline, it is expected that less NO_x will be produced.

2.1.2 Evaporative Emissions with Methanol

Evaporative emissions from vehicles burning pure methanol are relatively unreactive (i.e., they are composed of pure methanol). Evaporative emissions from alkane-methanol mixtures appear to be dominated by alkanes. For example, one report (CIT) uses the assumption that the evaporative gases from a 5.5% isopentane in methanol solution are 78% alkanes (by weight), or similar to the alkane content of gasoline vapors. This report shows that the methanol effectively replaces olefin and aromatic emissions with the alkanes remaining approximately the same. Thus, for alkane-methanol blends, while the vapors are "simpler," the percentage of the alkanes is deceptively high. Also on a carbon percent basis, where the alkanes (e.g., butane) are 85% carbon by weight and the methanol is only 38% carbon by weight, the ratio of alkanes in the vapors may be very high.

2.1.3 Exhaust Emission Rates for Regulated Pollutants

Table 2-1 summarizes exhaust emissions data from burning methanol in spark ignition engines using the Federal Test Program test cycle. All of the vehicles shown in Table 2-1 were carbureted except for the Rabbit, which was fuel injected. Table 2-1 is broken down into as many exhaust components as were published in the research literature. In some cases, the different components are not mutually exclusive. As shown, emission rates of hydrocarbon

TABLE 2-1. SUMMARY OF EXHAUST EMISSIONS DATA ON VEHICLES BURNING METHANOL

Reference: Lowry & Devoto, 1975

Vehicle/ECS	1947 CER engine, one-cylinder No Controls							
Operation	Ø = 1.0				Ø = 1.1			
	1000 rpm		1800 rpm		1000 rpm		1800 rpm	
Pollutant: g/hph	Methanol Fuel	Indolene Fuel	Methanol Fuel	Indolene Fuel	Methanol Fuel	Indolene Fuel	Methanol Fuel	Indolene Fuel
HC	1	2	0.8	1.8	1.6	2.5	1	2.3
CO								
NO_x	12	10	4.5	8	4	2	1	1.3

Reference: Hilden & Parks, 1976

Vehicle/ECS	Single-Cylinder engine, 0.60L ASTM-CFR					
	Ø = 1.0			Ø = 0.8		
Fuel	Methanol	Indolene	90% Methanol 10% H_2O	Methanol	Indolene	90% Methanol 10% H_2O
Pollutant: mg/mi						
NO_x	4 μg/J		2.5 μg/J	2.5 μg/J		1 μg/J
Aldehyde (F=formaldehyde)	0.1 μg/J	0.03 μg/J	0.1 μg/J	0.2 μg/J	0.05 μg/J	
Methanol (UBF)	0.5 μg/J	0.5 μg/J	6.3 μg/J	0.5 μg/J	0.5 μg/J	5.5 μg/J

Note: UBF = Unburned Fuel
Gas = Gasoline

... continued

TABLE 2-1. (Continued)

Reference: CARB, 1982

Vehicle/ECS	81 Escort				81 Escort				81 Rabbit			
	Baseline		No AIR or EGR	No CAT	Baseline	No CAT	Baseline	No CAT	Baseline	No CAT	Baseline	No CAT
Fuel	94.5% Methanol, 5.5% Isopentane				94.5% Methanol, 5.5% Isopentane		97.5% Ethanol, 2.5% Gasoline		94.5% Methanol, 5.5% Isopentane			
Test	81 test	82 test	81 test	82 test			81 tests		81 tests			
Pollutant: mg/mi HC	240	200	510	1,211	230	1,890	210	1,150	150	840	210	880
CO	4,770	3,020	23,500	28.300	6,630	51,000	1,280	10,540	1,330	12,620		7,320
NOx	410	170	740	490	240	1,010	530	2,490	200	1,060		2,310
Aldehyde (F=formaldehyde)	(F) 8.4	(F) 17	(F) 82.6	(F) 70	(F) 13	(F) 100	11 (F) 23	170 (F) 50	(F) 37	(F) 75	(F) 19	(F) 99
Methanol (UBF)	30	270	830	2,550	280	3,840	(UBF) 200	1,310 (UBF)	280	1,250	350	1,300
Methane	60	45	130	35	64	73	46	80	14	200	12	60

Reference: Brinkman, 1981

Vehicle/ECS	Single-Cylinder Engine							
	Ø = 1.0				Ø = 1.2			
	CR = 7.5	CR = 12	CR = 18	CR = 7.5	CR = 7.5	CR = 12	CR = 18	CR = 7.5
Fuel	Ethanol			Gas	Ethanol			Gas
Pollutant: mg/mi								
CO	0	0	0	0	45 μg/J	40 μg/J	35 μg/J	60 μg/J
NOx	3 μg/J	3 μg/J	3.3 μg/J	4 μg/J	0.5 μg/J	0.5 μg/J	0.5 μg/J	0.5 μg/J
Aldehyde (F=formaldehyde)	0.1 μg/J	0.2 μg/J	3.5 μg/J	0.05 μg/J	0.2 μg/J	0.25 μg/J	0.38 μg/J	0.05 μg/J
Methanol (UBF)	(UBF) 1 μg/J	(UBF) 1 μg/J	(UBF) 1 μg/J	(UBF) 1.5 μg/J	(UBF) 2 μg/J	(UBF) 2.3 μg/J	(UBF) 2.5 μg/J	(UBF) 2.3 μg/J

...continued

TABLE 2-1. Continued

Reference: Smith, Urban, & Baines, 1982

Vehicle/ECS	81 Escort/EGR/PMP/OXD/3-way/Fuel Metering				81 Rabbit/3-way Catalyst/ Closed Loop/MFI		
	Noble Metal	Promoted Base Metal	No Catalyst	Noble Metal	Noble Metal	Promoted Base Metal	Noble Metal
Fuel	Neat Methanol	Neat Methanol	Neat Methanol	Gasoline	Neat Methanol	Neat Methanol	Gasoline
Pollutant: mg/mi							
HC	420	310	10,280	370	390	480	110
CO	6,030	1,510	40,770	4,490	880	2,740	1,080
NOx	400	350	610	550	680	1,510	160
Aldehyde (F=formaldehyde)	(F) 34	(F) 3	(F) 356	(F)<1.6	(F) 9.7	(F) 32	ND
Methanol (UBF)	424	103	11,494	ND	440	542	ND
Particulates	6.5	3	11	9.7	4.8	6.5	12
Methane	48	35	66			11	14
NH_3	9.7	4.8	3				
CN	ND	0.16	0.16				
Organic Amines	0.016	ND	0.65				
MeONO ppm (Hrs)	0.5(12hr) 0.3(24hr) 0.5(48hr)				ND (ohr)		

Reference: Energy Conservation Directorate, 1982

Vehicle/ECS	78 Pinto, 2.3L Closed loop, enlarged jets		2.3L Pinto Turbo		
			Base Spark Timing	5% Spark Advance	
Fuel	Methanol	Indolene	Methanol	Methanol	Indolene
Pollutant: mg/mi					
HC	160	300	1,710	3,280	1,750
CO	2,610	2,510	38,100	37,400	26,400
NOx	680	980		1,150	3,940
Aldehyde (F=formaldehyde)	32	11			
Methanol (UBF)			850		
Methane				1,640	1,750

...continued

TABLE 2-1. Continued

Reference: Smith & Urban, 1982

Vehicle/ECS	Escort Noble Met	Rabbit Noble Met	Rabbit P.B.M.	Escort P.B.M.	Escort No Cat	(new Cat) P.B.M.	(new carb) Noble Met
Pollutant: mg/mi							
HC	(14.2 ppm) 420	(15.8 ppm) 387	(31.7 ppm) 871	306	10,306	484	468
CO	(203 ppm) 6,048	(41.4 ppm) 887	(133.6 ppm) 3,613	1,516	40,871	2,742	2,290
NO_x	(9.4 ppm) 403	(16 ppm) 677	(30.8 ppm) 1,758	355	613	1,516	403
Aldehyde (F=formaldehyde)	(F) 34	(F) 10.3	(F) 48	(F) 3	(F) 356	(F) 32	(F) 18
Methanol (UBF)	408	439	924	152	11,494	542	424
Particulates	6.5	4.6		2		6.5	5
Methane	48	4.8		35	66	11	
MeONO	<0.3 ppm 0.5 ppm	<0.3 ppm	4.1 ppm				

Reference: Edwards & Baisley, 1981	
Vehicle/ECS	78 Pinto 3-way catalyst
Fuel	Neat Methanol
Pollutant: mg/mi	
HC	110 - 220
CO	2040 - 3690
NO_x	610 - 760
Aldehyde (F=formaldehyde)	20 - 44

(HC) and carbon monoxide (CO) when burning methanol are similar to the rates of similar engines burning gasoline or Indolene (EPA's gasoline test fuel). Methanol generally is included as a part of HC emissions, although the overall emission mass, as HC, does not include the oxygen in the methanol. Methanol emissions usually account for a majority of HC emissions; in some cases, the methanol mass exceeds the total HC emissions (because of the oxygen).

CO emissions are sometimes greater when burning methanol than when burning gasoline; in other cases, they are greater with gasoline. Overall, for catalyst equipped vehicles, CO emission rates were relatively low with either fuel.

The reductions in NO_x emissions associated with burning methanol appear to be significant for pre-1980 model year vehicles, but the reduction appears to be low to nil for 1981 and newer vehicles (correctly operating). It is possible that the NO_x reductions associated with the three-way catalysts in 1980 and newer vehicles tend to mitigate the relative impact of burning methanol. In other words, the lower NO_x emission rate associated with the use of methanol is more significant when compared to the high rate of older, uncontrolled vehicles than when compared to the already low rate of newer, controlled vehicles. Unfortunately, the data base is very limited, particularly the data base comparing emissions from vehicles burning methanol with emissions from vehicles burning gasoline.

2.1.4 Exhaust Emission Rates for Unregulated Pollutants

The review of the literature indicated that the primary combustion product of concern was formaldehyde. Formaldehyde emissions varied between less than 1% and 40% of the total HC value (on a mass basis) with an average value of 9.3%. The 40% value was with a very rich air/fuel mixture. Aldehyde emissions (including formaldehyde) are at their lowest level at an equivalence, or air fuel ratio of 1:1 (Edwards, 1981). This result indicates that closed fuel control systems, which are expected to be used on most future light duty vehicles, will minimize formaldehyde emissions. Such closed loop systems tend to maintain an air-fuel ratio near 1:1, which corresponds to closed loop operation.

Published formaldehyde emission levels from catalyst-equipped vehicles burning methanol varied between 3 milligrams per mile and 48 milligrams per mile. For correctly operating catalyst-equipped vehicles burning gasoline, formaldehyde emissions varied between non-detectable amounts to 11 milligrams per mile. For vehicles without catalysts, or with disabled emission control systems that would reduce the catalytic converter efficiency, formaldehyde emissions were much greater for methanol fueled vehicles. In this case, formaldehyde emissions varied from 50 milligrams per mile to 356 milligrams per mile. Obviously the catalytic converter effectively reduces formaldehyde emissions. This could indicate that formaldehyde emissions could be excessive from tampered vehicles burning methanol. There were no comparative data on formaldehyde emissions from gasoline fueled vehicles with disabled or missing catalysts. However, formaldehyde emissions from a gasoline-fueled vehicle equipped with a three-way catalyst but with the feedback system disabled have been reported to be as high as 40 mg/mile (Wuebben, *et al*, 1982).

Other pollutants of concern include ammonia (NH_3) and methyl nitrite (CH_3ONO or $MeNO_2$). Smith, *et al* (1982) cited ammonia emissions of between 4.8 and 10.7 milligrams per mile for three-way catalyst-equipped vehicles burning methanol. Reference 14 included the results of sampling for methyl nitrite. The formation of methyl nitrite depends on the NO concentration and accordingly on the dilution of the exhaust gases. Methyl nitrite is not produced in the combustion chamber. Consequently, methyl nitrite emissions are measured by simulating post-combustion reactions in a dilution chamber after the tailpipe. The results shown by Southwest Research Institute (1982, Table 10) indicate that methyl nitrite varies from less than 0.3 ppm to 4.1 ppm. As a comparison, hydrocarbon emissions (including methanol) varied between 14 and 32 ppm. At this time, the data are not adequate to accurately project methyl nitrite emission levels from methanol-fueled vehicles. The above data only provide a very rough ballpark estimate of how much methyl nitrite will be produced.

2.2 Overall Requirements of Photochemical Mechanisms To Simulate Methanol Photochemistry

Photochemical reaction sets have been developed to simulate polluted urban air masses. Since methanol is not normally present to a significant extent in urban smogs, models do not incorporate it explicitly. However, with the introduction of methanol as a major fuel, substantial quantities of methanol and methanol combustion products will be emitted to the urban atmospheres. Although most mechanisms are capable of treating methanol chemistry through the use of surrogate species, additions should be made to the existing models to account for these new species.

First, any photochemical reaction set must be altered to accommodate the principal new species, methanol. As will be explained below, this addition is straightforward and well agreed upon. Accomodation of formaldehyde, the primary oxidation product of methanol other than CO_2, is a little more subtle. Most models already have some provision for dealing with formaldehyde since it is found in all urban smogs. Because it is a very important photochemical radical generator, the model must respond appropriately to unusually large increases in formaldehyde levels.

Methyl nitrite, a secondary product of methanol combustion, is emitted in only small amounts. However, methyl nitrite may be important if the model is sensitive to the number of radicals generated, since methyl nitrite is photochemically very reactive and forms radicals. Thus, models must add methanol and methyl nitrite chemistry and be able to accomodate the unusually large increase in formaldehyde.

The number, and possibly the mixture, of hydrocarbons, or more specifically, the non-methane organic compounds (NMOC), may change with substantial use of methanol fuel. The chemistry mechanism should therefore be validated over the expected ranges of NMOC concentrations and types of mixtures. Also, with lower NO_x emissions expected, the mechanism should be validated in the lower NO_x ranges. Since models are sensitive to NMOC/NO_x ratios, caution should be exercised when comparing results for different NMOC/NO_x ranges. However, if both NMOC and NO_x are expected to be reduced or unchanged, the NMOC/NO_x ratio may not vary drastically.

2.3 Review of Previous Methanol Studies

Both SAI and CIT have been working for a number of years in photochemical modeling. Their photochemical mechanisms were developed independently. Each mechanism has been validated against smog chamber runs similar to Los Angeles basin conditions and against actual Los Angeles area smog data. Comments on each report and their respective approaches to the methanol fuel chemistry modifications will be presented first, after which the specific results of the two studies will be compared.

2.3.1 Chemical Reaction Mechanisms Used

The SAI researchers used the photochemistry of the CBM-III model (Carbon Bond Mechanism—third version). While much of the validation for this mechanism has been done on CBM-II, most of it should be applicable since the SAI researchers state that the changes were minor and involved only the aromatic chemistry.

The CIT group has been working on photochemical smog mechanisms for several years, with specific attention to the Los Angeles basin situation. Their mechanism, called CIT in this report, has been developed essentially independently from other mechanisms and represents an equivalent but different mechanism from the SAI approach. It has been well-documented in the Los Angeles basin. While the internal dynamics of the two mechanisms are somewhat different, they are both based upon independent study reported in the literature. The predictions of the concentrations of the major species are similar in both mechanisms.

2.3.2 Methanol Photochemistry

The essential atmospheric chemistry of methanol is simple. Nearly all researchers agree (Dodge, 1984) that there is only one significant reaction and that is with the hydroxyl radical, OH:

$$CH_3OH + OH \longrightarrow HO_2 + HCHO \qquad (2\text{-}1)$$

Even the rate of this reaction is well agreed upon, and the inclusion of this reaction in any chemical reaction mechanism should be straightforward. Compared to most HC species, the methanol molecule is rather slow to react (its rate constant is about half that of butane). When it does react, as seen in equation 2-1, it generates radicals and formaldehyde. Therefore, it cannot be considered (or lumped) as a general hydrocarbon and must be treated as a separate species. Since all mechanisms contain OH and HO_2 radicals, they should easily be able to assimilate the newly introduced methanol reaction.

The CIT and SAI groups added essentially the same methanol chemistry, although CIT chose to represent it as a two-step reaction with CH_2OH (the hydroxy-methyl radical) as an intermediate. Since this radical reacts primarily with oxygen to form formaldehyde and the HO_2 radical (the same products as in equation 2-1 above), both approaches appear to be very straightforward and equivalent if not identical. The formaldehyde must be dealt with a little more carefully.

2.3.3 Formaldehyde Photochemistry

As seen in equation 2-1, formaldehyde is one of the products of atmospheric methanol reduction. It is also the second-most abundant product of methanol combustion. Therefore, considerable amounts of formaldehyde may be released to the atmosphere from methanol usage. Since formaldehyde is photochemically active to generate radicals, it is an important source of radicals in most mechanisms. Essentially all photochemically reactive models somehow take account of formaldehyde, but many assume that it will be present only in small quantities.

In CBM-III, all carbonyl groups (C=O) are lumped together and called CARB. They are given a rate constant which is a weighted average of typical mixtures of carbonyl groups. The weighting is dominated by formaldehyde. Since formaldehyde has assumed special significance in the current application, SAI has chosen to introduce formaldehyde explicitly into the mechanism. To do this, SAI introduced three additional, specific formaldehyde reactions into the mechanism, two of them photolytic reactions and the other, formaldehyde reaction with hydroxyl radical. They are essentially the same reactions that already exist in the mechanism for CARB, but their rate constants and products are specific for formaldehyde, rather than generalized, lumped carbonyl rate constants and products.

This procedure is the obvious and logical thing to do. The SAI team treats all other emissions as usual and classifies their emissions in terms of the normal CBM-III. That is, all formaldehyde emissions other than from on-road vehicles continue to be treated as before as part of the carbonyl bond catagory. Thus, the new reactions apply only to formaldehyde generated from methanol combustion.

The visible light that is photoreactive with NO_2 and the ultraviolet light that is photoreactive with formaldehyde scatter differently as they pass through the atmosphere. Therefore, the effective solar flux of the two different wavelengths is not simply proportional, but varies in a more complex manner. The resulting differences in the NO_2 and formaldehyde photochemical rate constants are not expected to be large, except perhaps at low sun angles where the scattering differences are largest.

In the SAI study, the photochemistry of the formaldehyde was not simply ratioed from the photolysis rate of NO_2 as is done for other photochemical rates. Rather, the algorithm of Demerjian and Schere (1979) was used. This algorithm takes into account both soler zenith angle and the spectral dependency of the formaldehyde photochemical reaction. The CIT mechanism also attempts to calculate solar flux difference due to spectral dependency. However, the spectral dependence algorithm used by CIT is much more complex than that used by SAI. In the first hour or two of daylight, when the sun angle is low, the CIT model would result in a lower, and perhaps better, formaldehyde photolytic rate constant. Since formaldehyde builds up during the nighttime, the rate of production of radicals in the early morning is important when determining the dynamics of the chemistry of the air mass. The CIT model may therefore be expected to be more accurate in simulating the actual early morning chemistry and photochemistry of formaldehyde.

The CIT mechanism does not lump all carbonyl group reactions together, but treats formaldehyde reactions independently from lumped higher aldehyde chemistries. Thus, no additional formaldehyde chemistry is needed. Since the CIT mechanism uses rate constants for the higher aldehyde reactions specifically chosen for these species, it may more closely represent the actual aldehyde chemistry than the modified CBM-III reaction set.

2.3.4 Methyl Nitrite Photochemistry

The CIT group did not address the effects of methyl nitrite chemistry. The reactions investigated by SAI are:

$$CH_3ONO \rightleftharpoons CH_3O + NO \qquad (2\text{-}2)$$

$$CH_3O + O_2 \longrightarrow HCHO + HO_2 \qquad (2\text{-}3)$$

The reaction rates used by SAI are: 0.3 times the NO_2 photolysis rate for the forward reaction 2-2, 4.4×10^4 ppm^{-1} min^{-1} for the back reaction, and 1.88 min^{-1} for reaction 2-3.

The formation of methyl nitrite in the atmosphere is poorly understood. It is questionable whether methyl nitrite would be present in quantities significant enough to make the above reactions important. However, methyl nitrite is highly photolytic resulting in the formation of HO_2 radicals. Because these radicals have a significant effect on ozone chemistry, SAI included reactions 2-2 and 2-3 in their study. Methyl nitrite was treated as an emission species from methanol fueled vehicles.

The SAI report showed that to assume 1% of total methanol related emissions to be methyl nitrite led to a small (3%) increase in peak ozone. If higher levels of methyl nitrite are assumed (e.g., 5%), the SAI report predicts the peak ozone is increased 10% over of that predicted with no methyl nitrite. This indicates that the expected emissions or resultant ambient levels of methyl nitrite should be carefully researched to verify that the lower emission level assumptions are accurate.

The only fate of methyl nitrite in the mechanisms reviewed is photodissociation into HO_2 radicals. That is, methyl nitrite can only be removed during daylight hours while there is sunlight to photodissociate the molecules. Consequently, substantial quantities of methyl nitrite would be expected to build up at night and result in another possible large source of radicals at first light. Formaldehyde also could have a similar fate. These methyl nitrite reaction products could therefore significantly influence ozone formation on the second day and subsequent days of an ozone episode.

The VOC (volatile organic compound) emissions schedule (SAI, 1983) gives some idea of the impact of the early morning potential radical population due to formaldehyde and methyl nitrite. VOC emissions during the nighttime (i.e., between 2000 and 0600 the following morning) sum to about 17 times the comparable emissions of the same species expected in the first daylight hour between 0600 and 0700. If it is assumed (to a first approximation) that the on-road/off-road (mobile and stationary) ratio of VOC emissions is maintained during the nighttime, the formaldehyde and methyl nitrite emissions during the night would be approximately 17 times the amount of the same species emitted in the first daylight hour.

Therefore, if all the nighttime formaldehyde and methyl nitrite emissions were present at dawn, the large and sudden generation of radicals would be expected to significantly affect the ozone production dynamics for the day. Radical populations and daily ozone dynamics (other than peak ozone) were not discussed in either report. Analysis of these populations and reaction dynamics could be expected to improve understanding of the role played by methyl nitrite in ozone chemistry.

Ozone formation is very dependent upon the number of radicals generated, and aldehydes are a principal source of radicals. For many models, once a certain level of radicals is reached that allows the mechanism "to get going," ozone formation becomes very much less sensitive to additional radical inputs. An early morning surge of radicals could have a major effect on the evolution of the air mass. Predicting just peak ozone for a day, which may not be a very sensitive indicator of the overall pollution, does not tell the whole story. For example, an early high radical population should considerably speed up the attainment of the ozone peak and result in larger overall (integated) exposure, but still not change the peak ozone very much.

2.3.5 Post-Study Validation Experiment

Since the publication of the two methanol studies discussed above, a smog chamber study has been completed involving methanol as one of the test gases (Whitten and Pullman, 1984). The principal result is the demonstrated importance of the non-methane organic compound-to-nitrogen oxides (NMOC/NO_x) ratio in controlling the formation of ozone. At low NMOC/NO_x ratios (3:1, ppm carbon:ppm NO_x), where there was little hydrocarbon, and using ozone generation as the indicator, methanol functioned almost as an inert species when it replaced hydrocarbons. At a 9:1 ratio, methanol was about half as reactive as the hydrocarbons it replaced. At high NMOC/NO_x ratios of 27:1, where the hydrocarbons are abundant, there was essentially no difference when some of the hydrocarbons were replaced by methanol. The authors state that the current NMOC/NO_x ratios in the Los Angeles basin are usually near the 9:1 ratio.

In the same study, upon further validation with the same smog chamber, the SAI mechanism was found to overpredict ozone at low NMOC/NO_x ratios. The problem was rectified by dividing the aromatic components into two classes. The authors further conclude that the new mechanism, Carbon Bond - IV (CBM-IV), should predict greater ozone reduction with methanol replacement, especially at low NMOC/NO_x ratios.

The CIT mechanism has not been subjected to any similar validation study involving methanol in smog chambers.

2.4 Discussion of SAI and CIT Results

Both studies used the same approach to make predictions about how the use of methanol as a primary fuel in automobiles would impact peak ozone levels in the Los Angeles Basin. They both went back to a well-documented, high-ozone episode and demonstrated that their model could adequately describe (i.e., could predict to within ten percent) the incident. They then took the same meteorological conditions and applied them to a day in the future where certain assumptions had been made about methanol usage and other emission inventories had been estimated. Because of all the assumptions necessary about background levels, meteorology and emission inventories, the results should be regarded only as approximate (accurate perhaps to a factor of two), and the details are not intended to be scrutinized for minor differences. The results are most useful for making comparisons with similar conditions (i.e., nearly identical previous days or the same day with slightly different input assumptions).

2.4.1 Base Case Results

Both studies chose their historical reference event to be an episode of high ozone which occurred June 26-28, 1974 near Uplands. The SAI team chose to model June 27, where an ozone maximum of 0.49 ppm was observed at Fontana at 1600 PST. SAI demonstrated the approximate equivalence of a trajectory and airshed model to predict the high ozone. They then used the same meteorology along with emission inventories projected for 1987 and modeled several different scenarios of methanol usage. The methanol emissions were spread proportionally over both on-road and off-road sources. Because use of methanol as a fuel may reduce the NMOC emissions and the NO_x emissions (methanol burns cooler and produces less NO_x), different amounts of NMOC and NO emissions were also studied. Some important results are assembled in Table 2-2.

TABLE 2-2. SELECTED RESULTS OF THE SAI STUDY

Methanol Usage (%)*	Other Changes From Base Case	Predicted Ozone (ppm)	Change From Base Case (%)	Change From 100% Case (%)
0	Base Case	0.27	0	-29
50	None	0.24	12	-14
100	None	0.21	23	0
100	No On-Road Sources+	0.19	32	10
100	50% NO_x Reduction	0.26	5	-24
100	50% NMOC Reduction	0.19	30	10
0	50% NO_x Reduction	0.31	-14	-48
0	50% Aloft NMOC	0.21	23	0
100	50% Aloft NMOC	0.15	44	29

* Methanol Usage refers to methanol replacing petroleum fuels in all on-road sources (spark-fired and diesel engines). Ten percent of the emissions (as carbon) have been assumed to be formaldehyde. Substitution is on a per carbon basis.

+ This calculation represents a theoretical lower bound of the ozone reduction assuming all on-road emissions were eliminated.

Source: (SAI, 1983)

It is important to note that the SAI model predicts that if the NO_x emissions are reduced the peak ozone will actually increase. Therefore, for the scenario where lower NO_x emissions accompany methanol usage, the SAI model predicts less reduction in peak ozone. The last two rows demonstrate that the peak afternoon ozone concentration is very sensitive to the background NMOC aloft concentration. The effect of methyl nitrite (1% of emissions as methyl nitrite) was small, about 3% increase in peak ozone. Again it should be pointed out that SAI felt that most of their assumptions were conservative so as to not overestimate the benefits of methanol conversion. For example, SAI assumed 10% of all emissions associated with methanol were formaldehyde and felt that they were probably overestimating the formaldehyde somewhat.

The SAI study did not report other components of the polluted air mass that might be affected by methanol conversion. For example, they did not give the concentrations of the major nitrogen sinks—PAN (peroxyacyl nitrate) and nitric acid. They reported only peak ozone and did not discuss the overall integrated or downwind ozone exposure. The SAI group did conclude that perhaps the most important dynamic described by the modeling is that the rather unreactive methanol replaces some of the relatively reactive hydrocarbons in the emissions. The removal of the reactive hydrocarbons is the primary cause of lower peak ozone when modeling methanol fuel use scenarios.

The CIT study used the adjacent day for their base case, June 28, 1974; on this day, the peak ozone observed was 0.38 ppm in Azuza at 1500 PDT. The CIT model predicted 0.37 ppm, but this day was one of the days used to "tune" the model, so the "prediction" should be quite accurate. The CIT group reported a more elaborate study of possible methanol use scenarios to estimate the emission levels of methanol and hydrocarbons. They focused on the year 2000, and in comparing several different studies of future vehicular activity, it was shown that there are significant differences in the ranges of predicted emissions. Selected results of their modeling are collected in Table 2-3.

TABLE 2-3. SELECTED RESULTS OF THE CIT STUDY

Methanol Usage (%)*	Other Changes From Base Case	Predicted Ozone (ppm)	Percentage Change from Base Case (%)
0	Base Case	0.33	0
50	None	0.30	9
100	None	0.29	14
100	50% NO_x Reduction	0.28	17
100	50% NO_x Reduction and 50% HC Reduction	0.27	19
100	All vehicular emissions Set to Zero	0.25	25

* Methanol Usage refers to methanol replacing gasoline in spark-fired engines; 21.2 weight percent of the exhaust hydrocarbon emissions were taken to be formaldehyde. Substitution is on a mass basis.

Source: (CIT, 1983)

2.4.2 Formaldehyde Emission Scenario Results

Because of the different target years and other assumptions, it is difficult to compare the absolute amounts of reductions and emissions. However, it is constructive to attempt to compare the percentage reduction used on each model for similar conditions. SAI assumed gasoline-to-methanol conversion of all on-road vehicles, whereas CIT assumed conversion of only spark-fired engines. (In Los Angeles, according to the CIT report, about 82% of all on-road emissions are produced by spark-fired engines.)

One of the scenarios considered by SAI assumed 100% methanol conversion of all on-road vehicles with no other hydrocarbon or NO_x emission reductions. For this scenario, SAI assumed that 10% (on a carbon basis) of the on-road methanol exhaust and evaporative emissions were formaldehyde. In addition, 4% of all other methanol emissions were assumed to be formaldehyde. These same assumptions, when applied to the CIT emissions inventory correspond to an assumption that approximately 12% of the gasoline exhaust emissions is replaced by formaldehyde (on a carbon basis).

Thus, the SAI scenario that assumed 20% of emissions as formaldehyde corresponds, approximately, to an assumption of 24% of emissions as formaldehyde using the CIT inventory. Therefore, the CIT scenario that assumed 21.2% of all gasoline exhaust emissions were formaldehyde does not exactly correspond to the SAI 20% emissions scenario.

These calculations consider weight percent versus carbon percent, the reports' assumptions about the relative amounts of off-road methanol emissions, and the reports' ratios of spark-fired to diesel engines. Even more subtle differences render any comparison approximate at best. These differences are due to blending assumptions, hydrocarbon species distributions and emissions along slightly different trajectories. Thus, given the rather broad limits and ranges of assumptions used by SAI and CIT, the 20% of methanol formaldehyde emission rate of SAI is roughly equivalent to the 21.2% of methanol formaldehyde emission rate of CIT. However, there is still considerable room for interpretation.

The SAI team assumed 10% formaldehyde emissions to be most reasonable, but they also calculated the peak ozone reduction assuming formaldehyde at 20% of the methanol-related emissions. This second case, given the discussion in the previous paragraph, approximately corresponds to the CIT assumption of 21.2% formaldehyde in emissions. In this case, SAI obtained only a 13% peak ozone reduction in place of the 23% reduction for 10% formaldehyde emission ratio; see Table 2-2. Their 13% result is very close to the 14% reduction reported by CIT for similar formaldehyde assumptions. To facilitate a very rough comparison between Tables 2-2 and 2-3, about 9% (or 0.024 ppm) should be added to the SAI ozone results to correspond with the higher (20%) formaldehyde emission assumption of CIT.

Both studies also calculated the theoretical limit where all on-road vehicular (or for CIT, all spark-fired vehicles) emissions are set to zero. At this extreme, the formaldehyde assumption is moot. The CIT result was a 25% reduction; SAI calculated a 32% ozone reduction.

2.4.3 Other Results

The CIT group also reported for the 100% methanol replacement of gasoline:

- a 21.5% reduction in PAN, and
- a 50% increase in ambient formaldehyde.

The PAN reduction was expected since the methanol-formaldehyde chemistry cannot lead directly to any PAN (no acetyl groups exist). The PAN reduction is certainly a beneficial result of methanol use since PAN is a major eye irritant. The SAI team judged the increased formaldehyde concentration to be of no acute consequence (except perhaps in closed areas such as garages), but the long-term effects of low exposure to formaldehyde are not well known.

In most mechanisms where light is present and NO_x is increased, the NO_x consumes ozone and the ozone concentration decreases. This rule is generally true in a typical polluted atmosphere. An exception to the above rule occurs at low NO_x or high hydrocarbon concentrations. The SAI results illustrate this response in their baseline case. Using a Level II EKMA trajectory analysis, ozone concentration increased from 0.22 to 0.26 ppm when NO_x was reduced 22% (Whitten and Pullman, 1984, Table 1). But when CIT reduced NO_x 50%, Case A to Case B with no other changes, ozone declined from 0.285 to 0.275 ppm. This is certainly not in a low-NO_x regime. Such behavior is a result of the many complex interactions within the model as a whole, and, while the result is not unreasonable, it does seem unusual.

Smog chamber results generally would favor the SAI results for a high NO_x case (Jeffries, et al, 1981). It should be noted, however, that in less polluted environments, where NO_x concentrations are lower, further NO_x reduction does result in reduction in peak ozone. This may make the strategy of methanol conversion more effective in environments less polluted, i.e., with lower ambient NO_x, than the Los Angeles Basin.

It should also be emphasized that the SAI study showed that the peak afternoon ozone concentration is sensitive to the background levels of NMOC, especially NMOC aloft above the mixing height. Gipson (1984), however, found limited sensitivity of peak predicted ozone to NMOC aloft concentrations. Gipson did find that the VOC control requirements were very sensitive to NMOC aloft concentrations. These studies show the benefit of long-term reductions in area-wide VOC emissions that contribute to reductions in NMOC background concentrations. Although the background NMOC level was not an issue in the present studies, future work, which attempts to produce quantitative results, should devote considerable effort to assessing appropriate background NMOC concentrations.

2.4.4 Summary of the Results of SAI and CIT Studies

Given the differences in the photochemical reaction sets developed and used by the two groups, it is perhaps somewhat fortuitous that the results should agree so closely when the same assumption about formaldehyde is made.

The key point to emerge in the results of the two studies reviewed is that the largest source of variation results from assumptions about input parameters into the models. Examples include assumptions about:

- the percentage of formaldehyde and methyl nitrite in the organic emissions,
- the effect of methanol on NO_x emissions,
- the concentration of background hydrocarbons,
- estimates about the amount of vehicular activity or the extent of methanol-for-gasoline replacement, and
- meteorology, emissions inventory, etc.

Thus, there is little in the results of the two studies to differentiate the two mechanisms. A consistent result is that, assuming about 20% of the organic emissions are formaldehyde, the use of methanol fuel would lead to approximately a 10-15% reduction in peak ozone for a high ozone episode in Los Angeles. Reduction of formaldehyde emissions below these levels would likely increase the percentage of ozone reduction. Other aspects of air quality would also be improved (e.g., lower PAN).

The dynamics of the air mass should be studied to more accurately assess the overall ozone exposure profile. The choice of chemistries may be less important than assumptions about formaldehyde emissions, ambient hydrocarbon concentrations and meteorology. As called for in both studies, smog chamber studies on methanol and formaldehyde are needed in order to validate the chemistries. Also, more studies are also needed to better establish the emissions (i.e., methanol, formaldehyde, NO_x and methyl nitrite) from methanol burning engines.

2.5 Consideration of Alternate Chemistries

When considering what mechanism to modify and use to predict the effect of widespread methanol usage on peak ozone concentrations, both methanol chemistry and the existing chemical mechanism must be looked at critically. Methanol chemistry is really quite simple. Methanol and methyl nitrite reactions may be added directly to existing mechanisms. These modifications are not expected to interfere with the existing chemistry reaction mechanism.

Another concern is formaldehyde. Formaldehyde is already in all existing mechanisms either explicitly or implicitly (i.e., as a lumped carbonyl bond or group). One must therefore simply make sure that the mechanism has the capability or capacity to deal with the higher formaldehyde levels expected to result from conversion to methanol. Most frequently, the mechanism will not have been validated in this increased formaldehyde (or aldehyde) range. The user should be alert for any possible "inconsistencies" that develop which may be attributable to the unusually high aldehyde concentrations.

The primary effect of aldehydes (and methyl nitrite) is that they are a source of radicals when the sun is shining. The number of radicals available to the mechanism greatly influences how that mechanism operates. Most reactive chemistry sets are very sensitive to concentrations of radicals. Therefore, the key factors in choosing a mechanism are how it will handle the increased formaldehyde concentration and how correctly sensitive and responsive it is to the population of radicals.

One of the first mechanisms to achieve widespread use was the Dodge mechanism (Dodge, 1977). This mechanism is relatively old and is used in the EKMA/OZIPP photochemical model developed for EPA. Many reaction sets have been proposed over the last several years to supplant the Dodge mechanism. None of them is clearly superior. The CBM-III is probably the most used and familiar mechanism. (CBM-II, probably the most validated mechanism, has now been superceded by a slightly improved version, CBM-III.) After CBM-III, the Demerjian mechanism has perhaps been most popular and does well with urban air masses (Demerjian and Schere, 1979). Finally, the CIT mechanism is a readily available newer mechanism consisting of 52 reactions.

The Demerjian mechanism was developed with a good deal of "artistry" and was tuned to urban plumes. It has, of course, been validated against smog chamber data. It achieves good results with some rate constants that were chosen to make the model work rather than chosen using the best or latest available laboratory data. For example, the Demerjian ozone-olefin chemistry generates significantly more radicals than current theories would suggest, but they improve the model's results (Jefferies, et al, 1981). The mechanism and its approach have been remarkably successful. However, because of the way it was constructed, one is uncertain if modification might upset some delicate balance.

The original Demerjian mechanism contained 37 reactions. A new version of the Demerjian mechanism is now available involving 63 reactions. If this mechanism performs as well as its simpler progenitor, it also should be a good candidate for use with methanol. It contains the two formaldehyde reactions explicitly (as well as higher aldehyde chemistry) and should be very easily adapted. It would need only the methanol reaction and, if desired, the methyl nitrite reaction.

Jeffries, Sexton and Salmi, in a comparative study of four chemical mechanisms against smog chamber and urban plume data from St. Louis, concluded that none of the mechanisms could satisfactorily predict the ozone actually measured in St. Louis for a ten day period (Jeffries, et al, 1981). All of the mechanisms considered (CBM-II, original Demerjian, CIT and Dodge) consistently underpredicted ozone. For example, CBM-II underpredicted ozone by greater than 25% on nine of the ten days studied. Both CIT and CBM-II mechanisms were believed to underpredict because of low radical input and because they are both somewhat oversensitive to radical availability. Both models also "greatly overrespond to HC compositional changes" (Jeffries, et al, 1981). The authors noted that on some days ozone reduction was approximately linear with reduced hydrocarbons. In essentially all cases, however, the ozone aloft was the most important factor in determining ground level ozone.

The reason for the poor performance of the mechanisms could not be specified in most cases, but uncertainties in meteorology, emissions, chemistry, trajectories, etc. all contributed to the disappointing results of the mechanisms. The contributions of the various chemistries to the poor predictions were impossible to quantify. Based on the comparative study, it appears that the best use of reactive photochemistry mechanisms at this time is to run the same mechanisms under similar conditions while varying only one parameter and observe the altered results. This type of sensitivity study is performed to a limited degree in Section 5.0.

The reader should therefore be cautious of considering any of the results in an absolute fashion; that is, one should not place great confidence in any single result, since any correlation with the real world may be somewhat fortuitous. However, when comparing results of nearly identical situations, where only one or two parameters have been changed, the relative results may be reasonably accurate, and the direction of change in some result (e.g., ozone concentration or PAN formation) should be correctly predicted. If several mechanisms predict the same type and magnitude of changes for similar situations, more credibility is given to the predicted responses.

Atkinson, Lloyd and Winges have published another photochemical mechanism which seems to be the most popular of the newer reaction sets (Atkinson, et al, 1982). If validation studies confirm its accuracy, it will be another candidate for the methanol study. However, it is a very complex mechanism and due to fractional and negative coefficients and a large number of species, it can not be directly substituted into most models. Formaldehyde is treated explicitly as is xylene.

Many of the other mechanisms have been developed for some special purposes (e.g., heterogeneous reactions, emission plume simulations) and have not been broadly validated. None of these other mechanisms would be expected to out perform the CBM-III, CIT, Demerjian, or Atkinson mechanisms.

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3.0 REVIEW OF PHOTOCHEMICAL MODELS

Section 2.0 investigated the applicability of various chemical reaction mechanisms for determining the air chemistry effects of switching spark-fired motor vehicles to methanol fuel. This section reviews readily available atmospheric transport and dispersion models. The models reviewed are those which could be used in conjunction with a photochemical reaction mechanism to quantitatively predict the atmospheric effects from such a fuel conversion.

In this review two recommendations will be made. One recommendation will be for the model most suitable for use in the Los Angeles Basin. The second recommendation will be for a model for use in arbitrary locations around the country. A recommendation is being made specifically for Los Angeles because of the special photochemical modeling problems that exist in the Los Angeles Basin and the unique emission characteristics and modeling history of Los Angeles.

3.1 Background

The model to be used for simulating atmospheric effects should, at a minimum, consider the following processes:

- Transport
- Dispersion
- Chemical Transformation
- Emissions

Besides these basic requirements, other processes can also be considered (such as deposition and vertical winds) to make the simulation more realistic. However, the more realistic the model is, the more stringent the data input requirements are. Thus, the selection of a model for a specific case should be determined by the type and amount of data which will be available for input. Lack of data forces approximations to be made for some of the input. A model which requires less input has already made internal assumptions for the processes not specifically modeled.

In this report eight models will be reviewed with the following criteria in mind:

- Physical basis (realism)
- Chemistry capability
- Emissions handling
- Input requirements
- Validation
- Documentation

Physical basis includes how the model considers transport and diffusion as well as other processes which add realism, and thus a better chance of reliable simulations.

It is possible that any model selected for use in future modeling studies may be required to simulate atmospheric processes during nighttime conditions. The ability of the models to simulate nighttime transport will be reviewed. It should be noted, however, that it is extremely difficult to construct accurate wind fields or air parcel trajectories for nighttime situations (and daytime situations in many instances).

Since there may be more than one chemical mechanism to be used, and chemical mechanisms change as knowledge increases, the models will be screened for their ability to modify the chemical mechanisms already contained within them.

The effect of altered emission profiles on ambient air quality is the main concern of the methanol study. Because of this, the way that emissions are handled by type, source characteristics, and temporal variation will also be reviewed. As already stated, the amount of data available for input should be a factor in determining the model to be used. If large data bases are required to formulate the input, and these data are not readily available, the model's usefulness is decreased.

Validation gives a measure of how well a model works. However, validation studies are only useful for predicting how the model will behave in similar situations. Thus, the variation and number of validations carried out is important. The final criteria, documentation, is probably the most important if the model is to be used by personnel other than the model developers. Without readily available documentation describing the details of the required input and limitations of a model, the general usefulness of a model is greatly reduced.

3.2 Models To Be Reviewed

In this study, two general model types will be reviewed: Eulerian and Lagrangian (or trajectory). The most widely used model type, Gaussian, is not included in the review because it cannot consider any but the most simple chemical reaction mechanisms. An Eulerian model considers a three dimensional grid set over a specific region. It is the most realistic in that it can consider physical processes in extreme detail. Because of its realism, an Eulerian model normally requires the largest amount of input. Eulerian models also normally require the largest amount of computer resources. The Eulerian models to be reviewed are:

- SAI Urban Airshed
- CIT Airshed
- MARC-1

Eulerian models can be used to predict concentrations over a large area as a function of time.

Trajectory models follow a single air parcel, which may be subdivided horizontally or vertically, as the parcel moves over a region. If the parcel passes over a source, it is affected. Other missed sources are assumed non-existent. Many assumptions are made as to horizontal and vertical dispersion and mixing with surrounding air parcels. All material within an air parcel or its subdivisions is assumed well mixed. It should be pointed out that this last assumption is also made for each grid box in an Eulerian model. A trajectory model usually has much simpler input requirements than an Eulerian model and requires much fewer computer resources.

Trajectory models predict the time history of concentrations for a single air parcel. Only concentrations at specific points along the parcel trajectory can be determined, and then only for the time at which the parcel passes over the point. It is possible to compute a trajectory so that the air parcel arrives at a site at the time of maximum observed ozone. However, to model an entire urban area, multiple trajectory model runs must be made, each run with a different trajectory. Also, for validation, each measuring station must generally be modeled separately since each station is usually affected by separate air parcels with different histories.

The trajectory models to be reviewed are:

- EKMA/OZIPM-2
- SAI Trajectory
- RPM-II
- GCKM/TRAJ
- STRATOS

The OZIPM-2 model is not a true trajectory model. Rather, it is more aptly classified as a "box" model, or a model where everything is assumed to occur within a stationary "box" or volume. For convenience, however, the OZIPM-2 model is discussed with the trajectory models.

3.3 Eulerian Models

Eulerian models are the most realistic models. These models can consider the effects of terrain and interactions of chemical constituents from one part of the grid on other parts. Eulerian models work at the differential level. That is, they can be made to look at as many processes as desired at any level of detail. However, the greater the detail the greater the input and computer resources required. Eulerian models can be made simpler by reducing the number of grid boxes, but the realism suffers. A box model consisting of one fixed box is, in principle, an Eulerian model but an extremely simple one.

The ability of a dispersion model to simulate nighttime transport is limited by the model's ability to accurately simulate nighttime wind flow. Because Eulerian models use detailed wind preprocessors to generate wind fields, Eulerian models are better able than trajectory models to simulate nighttime transport. The three Eulerian models reviewed in this section can be used to simulate nighttime transport given sufficient input data. The chemistry mechanism used is also a limiting factor when used in a model to simulate nighttime photochemical processes. This point is discussed in more detail in Section 4.0.

The Eulerian models to be reviewed here are existing models which have been used in validation or planning studies. All three models require extensive input data that does not exist for most locations. Los Angeles and a few other cities are exceptions in that extensive data bases exist for modeling photochemical processes in the Los Angeles Basin. Therefore, the review of Eulerian models is primarily intended to identify the most suitable model for use in Los Angeles and other cities with similar data coverage and modeling histories.

3.3.1 SAI Urban Airshed Model

The Systems Applications, Inc. Urban Airshed Model (Ames *et al*. 1978) is a multi-layer grid model with varying cell heights. The chemistry used in the model is a version of the Carbon-Bond Mechanism II (CBM-II) incorporating certain steady-state approximations. The mechanism is "hard-wired," or is built into the model. Documentation exists in two volumes: Ames *et al*. (1978) and Ames *et al*. (1979). The EPA has recently proposed inclusion of the Urban Airshed Model in the list of EPA Guideline models that are recommended for regulatory use (EPA, 1984).

Several versions of the Urban Airshed Model exist. However, only one version has been publicly released by EPA with accompanying documentation. Many potential difficulties associated with the publicly available version have been eliminated in more recent versions of the model. The EPA in the near future will release a revised version of the Urban Airshed Model including revised documentation. Even with the new version of the model, a prospective user will likely have to consult with EPA or SAI in order to ensure proper use of the model for a given application.

The model allows the use of temporally varying emissions from area and point sources. The allowed emitted species are those assumed reactive in CBM-II.

The input required by the Urban Airshed Model includes source and emission inventories, air quality boundary and initial conditions, and meteorological data (wind field, vertical temperature soundings, and NO_2 photolysis rates, relative humidity, and pressure). The emissions and meteorological conditions are to be given in an hourly schedule. The initial concentrations and meteorological conditions are required for each grid box.

This model has been compared with data taken in studies at Los Angeles (Whitten and Hogo, 1981; Reynolds *et al*. 1979), Denver (Reynolds *et al*. 1978), Sacramento (Anderson *et al*. 1977), and Tulsa (Hogo *et al*. 1981). The

EPA has summarized the results of these comparison studies (Layland and Cole, 1983). In general, the accuracy of the model can vary greatly depending upon the day simulated and the quality and amount of input data. Consistent, accurate results in predicting the peak ozone concentrations in place or time could not be achieved. Caution must be used when analyzing the results of these validations, however. Different versions of the models were used for some of the cities, and so exact comparison among the studies is not possible.

The use of any new mechanism would require changing the computer code. The degree to which the CBM-II mechanism is integral, or "hard-wired," in the code can only be assessed by a thorough study of the code. This existence of the integral CBM-II chemistry is one significant potential problem associated with the use of the SAI model.

Radian has reviewed the SAI model (Radian, 1981) for the Texas Air Control Board (TACB) and found several deficiencies with the model. The most serious was with the wind field. The SAI model expects to be given wind speeds and directions for each grid cell. A preprocessor is available (WIND) to perform this function. However, the winds developed by this preprocessor are average winds and are not necessarily consistent with the measured wind values. The winds developed in the final wind field often do not agree with the input wind data for specific cells. A certain amount of averaging which takes place in the preprocessor allows resultant wind data to potentially differ from the input data.

SAI has other wind preprocessors which it uses for specific locations. The necessity to have site-specific wind preprocessors greatly reduces the usefulness of the model in arbitrary locations. New wind preprocessor programs may have to be written if the model is used to model a new location.

During Radian's prior review of the Urban Airshed Model, several minor inconsistencies were noted between the user's manual and the model. Examples of these problems are that the units conversion option did not perform correctly, the user's guide has numerous discrepancies and oversights, and the coding is for an older version of FORTRAN and is not transportable to all other computer systems.

3.3.2 CIT Airshed Model

The CIT Airshed model is an Eulerian model developed at the California Institute of Technology. Only two references (McRae, et al, 1982, and McRae and Seinfeld, 1983) describe the CIT model in the open literature. No documentation is available of the details of input required. Telephone coversations with Dr. Seinfeld at CIT are the basis of some of the information presented here. The model is publicly available.

The model is best described as a research tool rather than as a model ready for widespread use by users with varying degrees of experience in modeling. This is the case for most large Eulerian models, and is not specific to the CIT model. However, of the three Eulerian models reviewed here, the CIT model is the most research-oriented of the three.

The chemistry mechanism in the model, the CIT mechanism, is presented in the two papers already cited. This mechanism is integral to the model. For the mechanism to be changed in the model, code changes are required. Some steady-state assumptions are made. This is not bad in itself, but usually forces some restriction on the order and relationships between the reactions.

The model considers both area and point sources. The point source emissions are allocated into the appropriate vertical cell after a plume rise calculation. Line sources are allocated over areas. Species dependent deposition rates are calculated for loss terms. Averaging is performed in the model to fill any missing data.

The input requirements are similar to those of all other Eulerian models. More detail as to input data requirements is not available without a user's guide. As already stated, adequate documentation is not available for the model. Without documentation, it would be difficult for anyone but CIT personnel to use the model.

Validation studies of the model have been carried out in the Los Angeles area (McRae and Seinfeld, 1983) with good results. The model has already been modified for use in evaluating of methanol fuel conversion in the Los Angeles area (CIT, 1983).

3.3.3 MARC - 1 Model

The MARC-1 model is a highly modular, three dimensional Eulerian grid model developed at Radian. The original version is described in Eltgroth (1982). Because of its modular nature, modifications to the MARC-1 FORTRAN code can be easily and quickly incorporated into the model.

The MARC-1 model is not in the public domain. It has been used by Radian personnel during the course of Radian Corporation's consulting service contracts. Modeling performed using MARC-1 would have to be arranged through agreement with Radian.

The grid cell dimensions in MARC-1 are allowed to vary over a wide range of length scales ranging from meters to kilometers. Diffusion rates are determined by the length scales specific to the problem being simulated. Thus, the MARC-1 model can be used in modeling dispersion from sources on a scale of meters up to the scale of large urban areas.

The chemical mechanism to be used in the simulation is treated as just another input with only minor restrictions on the actual mechanism used. The reactions are allowed to vary with temperature, ultraviolet light, total solar radiation, water vapor concentration, and aerosol surface area. Multiple dependencies involving several of the above factors can be handled in the existing model without modification. This chemistry handling is done by portions of the General Chemical Kinetics Module (GCKM), which is also existent in two other models to be reviewed here (GCKM/TRAJ and STRATOS). With the

GCKM module, no _a priori_ assumptions are made on the details of the mechanism. The ability of MARC-1 to readily accept almost any chemical mechanism without modification is a major strength of the MARC-1 model.

Emissions are allowed from area and point sources. The emissions are temporally variable with any frequency. Line sources are not explicitly allowed, but must be allocated over an area. Point and area source input data format is relatively simple and straightforward.

The input requirements are similar to those of all other Eulerian models. However, the input processors were designed using the assumption that full data coverage is not available. All missing data are estimated using inverse square averaging techniques on the data that is supplied. Because of this capability, MARC-1 can be used with as much or as little data as are available. Of course, the better the data coverage the better the results can be expected to be.

The MARC-1 model is the merger of three other individually validated models: IMPACT (Fabrick _et al_, 1977), PHOENIX (Eltgroth and Hobbs, 1979), and GCKM (Eltgroth, 1981). Each of the three component models in MARC-1 have been through validation studies separately. The major weakness of the MARC-1 model, however, is that it has not been validated as a unit on the scales (urban) that would be of interest for determining methanol impacts.

IMPACT has been tested in the dispersion of inert materials from point sources (Ranzieri _et al_, 1979; Sklarew _et al_, 1980, Fabrick and Haas, 1980; Taylor _et al_, 1981; and Fabrick _et al_, 1982). In these trials, IMPACT proved itself very capable of simulating the real world. It performed best when it had the best data coverage.

PHOENIX, in validation studies at eight coal-fired power plants, has been shown to be able to predict gas and aerosol transformations and interactions in plumes mixing with ambient air (Eltgroth and Hobbs, 1979; Hobbs _et al_, 1982a; Hobbs _et al_, 1982b).

The GCKM module used in the MARC-1 model is a very flexible module used to simulate chemical reactions. It uses most arbitrary chemical mechanisms. GCKM accepts a user-defined chemical reaction mechanism and calculates the time history of chemical concentrations. Reaction rates are allowed to vary with meteorological and pollutant variables. GCKM has been used to successfully simulate smog chamber experiments. The GCKM simulations compare very favorably with simulations performed using models with integral reaction mechanisms (Eltgroth, 1981; Eltgroth and Sedenberg, 1983 a and b).

Modifications to GCKM sometimes need to be made to run specific mechanisms. These modifications are generally simple and only involve allowing an additional dependency, or combination of dependencies, to be used to compute rate constants.

Most of the documentation for MARC-1 is present in Eltgroth (1982). Other recent changes to the model allowing the use of small-scale simulations and deposition are found in Radian internal reports available from Radian.

The lack of overall validation in similar projects (urban source ozone impacts) and the fact that MARC-1 not in the public domain seriously detract from its desirability.

3.4 Trajectory Models

Trajectory (or Lagrangian) models are an alternative to Eulerian models. Data requirements for a trajectory model are normally much less than those for an Eulerian model. The amount of computer time and memory required by a trajectory model is also less than that of an Eulerian model. The drawback of a trajectory model is that each run simulates only a portion of the region of interest. A trajectory model also gives the concentration time history of an air parcel rather than of a fixed site. The concentrations in the air parcel only correspond to the concentrations of a fixed site when the air parcel moves over the site.

Trajectory models normally ignore terrain. Whether or not an emission source affects the air parcel and is involved in the simulation depends totally upon the trajectory. The influence of a given source on the air parcel can be calculated by the user or by using objective techniques in the model.

A major drawtrack of trajectory models is their inability to simulate the effects of wind shear on the modeled air parcel. Wind shear effects are very important at night and under many stations during the day. Because the occurrence of wind shear effects both transport and dispersion, the inability to simulate wind shear is a major problem associated with the use of trajectory models.

The ability of trajectory models to simulate nighttime trajectories is limited and will be discussed. Usually, trajectory models are limited in their ability to simulate nighttime transport by the ability (or lack of it) of the model to accurately simulate nighttime trajectories. Some trajectory models cannot be used for simulating nighttime transport without the use of supplemental wind processors to compute trajectories.

The trajectory models to be reviewed are existing models which have been used in ozone assessment simulations.

3.4.1 EKMA/OZIPM-2 Model

The Empirical Kinetic Modeling Approach (EKMA) (EPA, 1977; and Gipson et al, 1981) is probably the most widely used methodology for simulating ozone impacts due to emissions. EKMA analyses are performed using the Ozone Isopleth Plotting Package (OZIPP) model (Whitten and Hogo, 1978a). The latest version of the EKMA/OZIPP model, Ozone Isopleth Plotting with Optional Mechanisms/Version 2 (OZIPM-2) (Gipson, 1984), is the model reviewed here. The OZIPP and OZIPM-2 models are both publicly released models.

The chemistry in OZIPM-2 is more flexible than that in the original OZIPP model. However, the model is still designed around the CBM-III chemical reaction scheme. For example, specific species names must be used for certain species and certain photolytic reaction rates are integral to the code. Thus, it is still difficult to alter or expand the mechanism for an arbitrary reaction mechanism. The addition of the required methanol reactions to CBM-III is not difficult.

In OZIPM-2, the air parcel is assumed to be of constant horizontal dimensions with a time-varying depth. The emissions can be entered either as hourly values of fractions of initial concentrations or as mass emission rates. The species splits (how much in each bond category) is an input to the model. Species splits, or carbon fractions, are assumed to be constant for a given simulation. The specification of emissions as concentrations eliminates the need of the model to consider how the horizontal dimensions of the air parcel change with time. However, since volume changes affect the concentrations in the air parcel, the parcel's horizontal and vertical dimension fluctuations must be considered when determining the initial concentration fractions which represent emissions.

The standard EKMA simulation (whether using OZIPP or OZIPM-2) assumes a straight-line trajectory. This type of simulation is termed Level III. As an option, the user may calculate a trajectory and have the trajectory's path determine which emission will affect the moving air parcel. The user then assigns these emissions to the air parcel as if the parcel trajectory were a straight line crossing each of the identified sources. This is termed a Level II analysis.

The OZIPM-2 model, when used in a Level III analysis, cannot simulate nighttime transport. If used in a Level II analysis, OZIPM-2 can be used for nighttime simulations if an appropriate trajectory preprocessor with adequate input data is used.

No single preprocessor has been designated for determining the trajectory path in Level II analyses with OZIPM-2. It is up to the user to perform this calculation. The South Coast Air Quality Management District (SCAQMD) is currently performing a Level II trajectory analysis using OZIPM and trajectories computed using the CIT Airshed model wind preprocessor (Liu, 1984).

Level II analysis with the use of CBM-III has been validated in studies performed by the South Coast Air Quality Management District (Liu, 1984). Multiple trajectories were calculated assuming a range of errors possible in the wind measurements. The envelope described by the multiple trajectories determined which emission sources would be included in the simulation.

The input required to run EKMA/OZIPM-2 are:

- Initial conditions
- Reaction mechanism
- Location (for light intensity calculation)
- Mixing heights
- Ozone and precursor transported values
- Emissions as initial concentration fractions or mass emission rates

This input data requirement is much less intensive than that for an Eulerian model and thus makes the model available for use in many more cases than an Eulerian model. In fact, other than wind and perhaps stability data, the input required for OZIPM-2 may be all that is available for a given typical modeling problem. Thus, for many situations, OZIPM-2 is more readily used than is an Eulerian model.

Because OZIPP and OZIPM-2 are so widely used, they have been involved in many model inter-comparisons and validations. In comparisons with field data it was indicated that OZIPP was not always reliable for predicting absolute concentrations of ozone (Jeffries _et al_, 1981, and Gipson, 1982). In fact, Gipson (1982) found that putting more effort into eliminating uncertainty in the input data (using Level II instead of Level III analysis) instead of using simplifying assumptions worsened the agreement between modeled ozone concentration and observed ozone data. While the limited cases analyzed by Gipson may not be representative for all modeling situations, they indicate that increased model sophistication may not be warranted in all circumstances.

The documentation for OZIPM-2 is plentiful (EPA, 1977; Gipson _et al_, 1981, and Gipson, 1984. The documentation includes discussions of the methodology for calculating default values for missing input data.

3.4.2 SAI Trajectory Model

The SAI Trajectory model (Reynolds _et al_, 1979) is a subset of the SAI Urban Airshed model. The major differences between the two models, in terms of input, computations, and predictions along a specific trajectory, are the elimination of horizontal dispersion, convergent and divergent winds, and the use of surface winds only for trajectory calculation. Potential users would have to obtain the SAI Trajectory model from SAI.

Because of the similarities, the general findings in the review of the Urban Airshed model also hold for the Trajectory model. In comparisons between these two SAI models, it was found (Whitten and Hogo, 1981) that the Trajectory model is often more in agreement with the observations than the more complex Urban Airshed model.

3.4.3 RPM-II Model

The SAI Reactive Plume Model, Version II, (RPM-II) (Stewart _et al_, 1980), assumes the air parcel consists of five cells, each of which is uniformly mixed in the vertical and arranged across the plume or trajectory. Each cell extends from the surface to the mixing height. The background concentrations surrounding the trajectory can be calculated by the model. Mixing with the air above and to the sides of the trajectory as well as between cells is allowed. The RPM-II model is publicly available.

RPM-II uses the CBM-II chemical reaction mechanism. This mechanism is integral to the model. Assumptions specific to the CBM-II chemistry and involving steady-state solutions are found throughout the model. Thus, modification to include methanol and updated reactions is difficult.

Point sources are the only emission sources allowed to influence the air parcel. Area and line sources are not considered.

The input data required are:

- Wind speed
- Plume width and depth or stability class
- Ambient and initial plume concentrations
- Point source emission rates and locations
- NO_2 photolysis rates

The trajectory in the model is assumed to be a straight line. To perform a Level II modeling analysis using RPM-II, trajectory preprocessing would have to be performed to determine which point sources are intersected by the trajectory and at what downwind locations. Because of the straight-line trajectory assumption inherent in RPM-II, the model could not be used to simulate nocturnal trajectories without use of a trajectory preprocessor.

Comparisons of RPM-II with field data have been carried out (Yocke et al, 1980; and Stewart and Liu, 1981) with good results. However, the data sets used for comparison were incomplete (no hydrocarbon data) and the missing data were tuned for best fit. According to a sensitivity test (Tesche and Roth, 1976), the parameters to which RPM-II is most sensitive are, in order:

- Background hydrocarbon concentrations
- NO_2 photolysis rates
- Background NO_x concentrations
- Background ozone concentrations

This sensitivity makes it difficult to assign a reliability to the field comparisons.

Documentation is available (Stewart et al, 1980). The documentation is clear and accurate.

The model's calculation of the concentrations in the air surrounding the trajectory lends an extra amount of realism to the model. However, this option is only useful in clean backgrounds with a point source plume, not in urban areas, and therefore it would not be useful for mobile source applications.

3.4.4 STRATOS Model

STRATOS is a highly modified refined version of ELSTAR (Lurman, 1979), a model developed by Environmental Research and Technology (ERT). The STRATOS model was developed by Radian Corporation. It is publicly available.

The STRATOS model is a multi-layer air parcel model which computes a trajectory path, allocates emissions as a function of time to the air parcel, and computes the concentrations in each layer of the parcel as a function of time (Balentine et al, 1984). It is designed to perform detailed Level II modeling analyses.

The chemical kinetic mechanism solver of STRATOS is the same GCKM module as that in MARC-1 (Section 3.3.3) and GCKM/TRAJ (Section 3.4.5). STRATOS has essentially no restrictions on which chemical mechanism may be used.

STRATOS considers both point and area sources. The sources are defined on a grid. If the trajectory comes in contact with a grid cell containing a source, that source is assumed to emit into the parcel. Plume rise calculations are done for point sources to place the emissions into the proper layer. In this respect STRATOS is very much like an Eulerian model.

The amount of input required is quite extensive and includes:

- Air parcel and grid sizes
- Layer dimensions
- Wind data
- Location
- Initial concentrations
- UV and water vapor data
- Temperature soundings
- Surface roughness
- Horizontal diffusion
- Deposition rates
- Rural emissions
- Point and area sources
- Reaction mechanism

Because of the extensive data requirements of STRATOS, creation of input data files can be difficult and time-consuming. In this respect, STRATOS is similar to the previously reviewed Eulerian models.

STRATOS has been partially validated for the Philadelphia area (Radian, 1984). The results showed good agreement between the model and the data. However, much of the required input was missing and "best guesses" had to be provided. In sensitivity testing, peak predicted ozone concentrations were found to be very dependent on the trajectory selected. Since the trajectory determines the emissions, this is no great surprise. This sensitivity of model results to the uncertainty in the trajectory is common for all trajectory models.

The documentation for STRATOS (Balentine et al, 1984) is complete with examples. The documentation has to be followed to the letter because many of the inputs follow different rules as to the number of inputs required or maximum or minimum numbers allowed. This can make preparing the model input difficult.

STRATOS is actually three programs. The first computes the trajectory path, the second allocates emissions, and the third computes the concentrations in each layer. This is the same breakdown as that contained in the GCKM/TRAJ model discussed in the next section. However, STRATOS assumes that the air parcel contains five vertical layers while the simpler GCKM/TRAJ model assumes an undivided air parcel. Also, the STRATOS model allocates emissions to the air parcel in a much more complex manner than that used in GCKM/TRAJ. Both models use portions of the first program, called METMOD, for trajectory calculation.

METMOD uses wind speed and direction values as functions of height, time, and location to give a composite trajectory path. Wind data for up to five vertical layers can be input into METMOD. The winds are weighted in the vertical for determining the air parcel path. These weights are supplied by the user and give the capability of weighting winds at some altitudes more than others. METMOD makes STRATOS and GCKM/TRAJ somewhat unique for trajectory models in that a very sophisticated, multi-level trajectory module is used to compute for the air parcel trajectory without using separate trajectory preprocessors. The METMOD preprocessor can construct realistic nocturnal trajectories if enough meteorological data are available.

3.4.5 GCKM/TRAJ Model

The Radian-developed General Chemical Kinetics Model with Trajectory Option (GCKM/TRAJ) (Balentine *et al*. 1984) is a single air parcel trajectory model capable of performing Level II modeling analyses. An option allows the user to consider horizontal air parcel dispersion as a function of stability class and wind speed. The user defines the depth of the air parcel with time.

The model is composed of three modules. The first module calculates the trajectory path, the second allocates emissions to the trajectory, and the third calculates the chemical concentrations in the air parcel as a function of time and distance.

Radian has not released the current version of the GCKM/TRAJ model to the public domain. An early version of the model without the trajectory and emissions preprocessors is in the public domain. Radian is presently supplying an executable version of GCKM/TRAJ to the Louisiana Department of Environmental Quality and EPA Region VI.

Trajectories in GCKM/TRAJ are computed using the METMOD wind data preprocessor of the STRATOS model. METMOD is discussed in more detail in Section 3.4.4. A significant feature of GCKM/TRAJ is that trajectories needed for performing Level II analyses can be computed without recourse to other trajectory preprocessors as is needed with OZIPM-2 or RPM-II.

Validation studies have not been competed for GCKM/TRAJ. A validation study is currently underway to validate GCKM/TRAJ for use in southern Louisiana (Baton Rouge). As discussed in Section 3.3.3, the GCKM chemical kinetics solving module contained in GCKM/TRAJ has been validated using smog chamber studies (Eltgroth, 1981). In addition, the METMOD trajectory model was used to compute the trajectories used in the successful partial validation of STRATOS for Philadelphia (Radian, 1984).

The model allows emissions from point and area sources. Using input from the METMOD trajectory preprocessor, a second preprocessor called EMIT computes which sources will interfere with the air parcel. For area sources, EMIT allocates some fraction of the area source emissions to the parcel, dependent on the amount of area source actually traversed by the parcel. Mobile and stationary area sources are treated separately. Mobile source emission factors dependent on the time of day can be entered to allow mobile source emissions to vary during the day.

The chemistry portion of the model (GCKM) is the same as that used in the MARC-1 model described in Section 2.3. GCKM/TRAJ will therefore accept a user-defined reaction mechanism with reaction rate dependencies on:

- Temperature
- Ultraviolet light
- Total solar radiation
- Water vapor concentration

The input required to run GCKM/TRAJ is:

- Surface wind data
- Wind soundings
- Vertical wind weighting scheme to determine trajectory
- Parcel size
- Stability class
- Initial and boundary concentrations
- UV, TSR, water vapor and temperature schedules
- Reaction mechanism

The documentation for GCKM/TRAJ consists of an up-to-date, relatively thorough User's Manual.

3.5 Summary and Recommendations

A summary of the review of the models is shown in Table 3-1. The models are evaluated on the six criteria:

- Physical basis (realism)
- Chemistry capability
- Emissions handling
- Input requirements
- Validation
- Documentation

This table only recaps the reviews found in Subsections 3.3 and 3.4.

3.5.1 Recommendation of Model for Los Angeles

The Los Angeles area presents a very complex problem for studying the effects of emission changes. Los Angeles has been extensively studied (SAI, 1983; and CIT, 1983). Emission and meteorological data bases are available.

Because of the complexity of the situation and the availability of data, an Eulerian model seems to be advisable. Of the three Eulerian models reviewed, two have been used to simulate the Los Angeles area: Urban Airshed Model and CIT Airshed Model. Of the two models, the Urban Airshed Model is the preferred model because of the existence of documentation and its proposed specification by the EPA as a guideline model.

Even with the existing documentation, it would be difficult to use the Urban Airshed model without direct aid from SAI on preparing wind field and area source input data. Preprocessors to perform these calculations exist

TABLE 3-1. SUMMARY REVIEW OF MODELS

Model	Physical Basis	Chemistry	Emissions	Input	Validation	Readily Available Documentation
SAI Urban Airshed	Eulerian	CBM-II	Point Area	(1)	Yes, L.A. and various urban areas	Yes, but incomplete; revised documentation in preparation
CalTech Airshed	Eulerian	CalTech	Point Area	(1)	Yes, L.A.	No
MARC 1	Eulerian	User[3]	Point Area	(1)		Yes
EKMA/ OZIPM-2	Trajectory	CBM-III	Not Specific	(2)	Yes	Yes[5]
SAI Traj.	Trajectory	CBM-II	Point Area Line	(1)	Yes, L.A.	Yes, but incomplete
RPM-II	Trajectory	CBM-II	Point	(2)	No	Yes
GCKM/ TRAJ	Trajectory	User[3]	Point Area[4]	(1)	No	Yes
STRATOS	Trajectory	User[3]	Point Area	(2)	Yes, partial validation for Philadelphia	Yes

1 - Eulerian type input: terrain, 3-D wind field, 3-D concentrations, emissions, met state parameters.
2 - Trajectory type input: wind speed, initial concentrations, emissions, met state parameters.
3 - User specifies reaction mechanism to be used.
4 - Area sources composed of stationary sources and mobile sources are handled separately.
5 - A user's manual for EKMA/OZIPM-2 using the CBM-III mechanism is being written by G. Gipson at EPA/OAQPS.

for Los Angeles since the model has already been used for such a simulation. These preprocessors and information on how to operate them could presumably be obtained through SAI.

A drawback of the SAI Urban Airshed model is the fact that the CBM-II chemistry is integral to the model. Thus, in order to perform simulations using other mechanisms, the user would have to make potentially extensive modifications to the model.

The second model to be recommended for use in Los Angeles is OZIPM-2 to perform a Level II EKMA trajectory analysis. This trajectory model has been shown to operate well in the area (Liu, 1984). OZIPM-2 has two drawbacks. First, the user will be required to determine the trajectory path and which emissions affect the trajectory. The SCAQMD is currently using the CIT Airshed model wind preprocessor to generated trajectories for use with OZIPM-2. Second, the OZIPM model is designed around the CBM-III chemical mechanism. Modifications to OZIPM would be needed to use alternative mechanisms.

The third model to be recommended for the Los Angeles area is MARC-1. The reason for this selection is that the model is a flexible model and is well-documented. MARC-1 is not restricted to use of a single chemistry mechanism. In addition, MARC-1 contains most of its own preprocessors for wind field calculation and source allocation. However, major effort would be required in preparing the input files.

The MARC-1 model would be second in the recommended list except for the serious drawback that it has yet to be validated as an entire model. The submodels from which MARC-1 was created, however, have been successfully validated separately. If the model is validated in the future in the Los Angeles region, its recommendation would increase to second.

Because of the lack of documentation, users of the CIT Airshed model would have to rely too heavily on its developers for assistance. In addition, the CIT model contains the CIT chemistry mechanisms integral to the code. As discussed in Section 6.3, the CIT mechanism is not a recommended mechanism for use in future studies of methanol photochemistry until the difficulties identified in Section 5.0 are resolved.

The recommended models for use in the Los Angeles area are, then, in order:

1. SAI Urban Airshed
2. Level II EKMA using OZIPM-2
3. MARC-1

3.5.2 Recommendation of Model for Other Areas

Four models are recommended for use in areas outside of Los Angeles. The model to use in a specific case is determined from the data coverage. The models recommended are:

Urban Airshed Model - High coverage of emissions, upper air, meteorological and air quality data.

STRATOS - Moderate coverage of upper air, meteorological and air quality data.

GCKM/TRAJ - Areas where Level II analyses are needed but only minimum data are available.

OZIPM-2 - All other minimum data coverage areas.

Selection of a model for an arbitrary location must consider the amount of input data that may be available. At a minimum, basic meteorological wind data (upper air and surface) and emission data (location and emission rates) will be assumed to be available. The emission data may not be speciated as to hydrocarbon classes. No matter which model is selected, some estimate of speciation will be required to allow use of the chemical reaction mechanisms being considered.

The consideration of data coverage leads to two model recommendations. The first recommended model would be for use in simulation of a region which is well-characterized as to emissions, meteorology, and air quality (surface and aloft). In this case, the Eulerian Urban Airshed Model would be recommended.

Where data coverage is sparse, the use of an Eulerian model would likely not be warranted since a number of simplifying assumptions would have to be made in order to run the model. These assumptions may lead to solutions, at a greatly increased cost, no better than the trajectory models which have many assumptions built in. Thus, a trajectory model would be recommended for this case. Three models are recommended, depending upon the relative degree of data coverage and the type of analysis to be performed.

Discussion of Recommendation for Data Rich Area

The Urban Airshed Model is the recommended model for use in an arbitrary location with excellent data coverage. There are two primary reasons for this selection. First, the model is proposed as a guideline model by EPA. Second, it has been extensively validated. However, as noted earlier, different versions of the model were validated. Therefore, the validation results may not be exactly transferable to the revised version likely to be used in future analyses.

There are two potential difficulties involved with the Urban Airshed Model. First, the model is presently restricted to use of the CBM-III mechanism. Second, input data preprocessors may have to be developed if the model is used in locations where it has not previously been used.

The MARC-1 model does not have the two above limitations. However, due to the lack of validation of MARC-1, the model is not recommended as the primary model for use in data rich areas. If at some point, MARC-1 is validated for use in a given location, the MARC-1 model should be considered for use in future modeling for that location.

The CIT Airshed model is also not recommended for two reasons. First, the CIT Airshed model, like the SAI Urban Airshed model, uses a chemistry mechanism (CIT) integral to the model. Second, the CIT model is not well enough documented for non-developers to be expected to operate the model.

Discussion of Recommendation for Data Poor Area

One of the major concerns of a trajectory model selection is the model's ability to use chemical reaction mechanisms which may be altered as knowledge increases. Two trajectory models have only very limited restrictions on the chemistry used since the user supplies the reaction mechanism as an input to the model. These are GCKM/TRAJ and STRATOS. In fact, the GCKM/TRAJ model is the model that was used, without modification, to perform all the sensitivity analyses discussed in Section 5.0. These sensitivity analyses involved using methanol-modified versions of the CB-III, Demerjian, and CIT mechanisms (see Section 4.0).

The SAI Trajectory model has the same problem with the wind field calculation as the SAI Urban Airshed model. Due to its integral mechanism and the wind field problem, it too is eliminated from recommendation. This leaves only the two trajectory models GCKM/TRAJ and STRATOS, for use in performing Level II analyses.

The selection of which of these two models to recommend for use in performing Level II analyses is once again dependent on data coverage. If chemical concentration data are available for heights up to the mixing depth, STRATOS is recommended. If only surface data, or limited upper air concentration data are available, GCKM/TRAJ is recommended.

For performing a Level III analysis, the EKMA/OZIPM-2 model should be used. OZIPM-2 is in wide use and has been extensively documented and validated for use in performing Level III analyses. Because of its widespread application for regulatory purposes, OZIPM-2 is recommended for data poor analyses where Level III analyses are sufficient. A drawback of OZIPM-2 is the requirement to use the Carbon Bond (or related) series of chemical mechanisms in the model. If a chemical mechanism other than CBM-III is used, the GCKM/TRAJ model can be used to perform the Level III analysis.

RPM-II would require alteration to consider a chemical reaction mechanism other than the one already residing in the model (CBM-II). The extent of alteration required would not be known until a thorough review of the actual code was performed. In addition, RPM-II is designed for use in modeling point source emissions only. Therefore the RPM-II model is not being recommended.

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4.0 MECHANISMS REVIEWED

4.1 Selection of Chemical Mechanisms

Five chemical reaction mechanisms which simulate ozone formation were considered for evaluation in the sensitivity analysis. These included:

- Dodge (Dodge, 1977)
- Carbon Bond III (Killus and Whitten, 1982)
- California Institute of Technology (CIT) (McRae, *et al*, 1982)
- Demerjian (Schere and Demerjian, 1977)
- Atkinson, Lloyd, Winges (Atkinson, *et al*, 1982)

Of these, Carbon Bond III, Demerjian, and CIT were selected for evaluation.

The Dodge mechanism was excluded from further analysis for three reasons. First, the Dodge mechanism is not considered to be an up-to-date mechanism. Second, it cannot readily handle the changes in reactivity (species composition) which were necessary for the sensitivity analyses. Finally, model runs identical to those runs for the other mechanisms in the sensitivity analyses would not be possible because of the reactivity limitations in the Dodge mechanism.

The Dodge mechanism, which is contained in EPA's EKMA/OZIPP model, assumes a VOC mix of 25% n-butane and 75% propylene plus an additional 5% as aldehydes. This composition is a surrogate composition derived only to fit the Bureau of Mines smog chamber results from which the mechanism was developed. The actual chemical species in an emissions inventory or polluted air mass cannot be explicitly assigned to these surrogate VOC classes. Therefore, changes in vehicle exhaust composition cannot readily be handled without invalidating the mechanism.

The Atkinson, Lloyd, Winges mechanism was excluded primarily because it is generally unavailable to the public and it is complex. This mechanism is contained within the Environmental Research and Technology (ERT) ELSTAR model. The mechanism contains several photolytic reactions which are not explicitly contained in the other mechanisms considered. It also utilizes a lesser degree of lumping of VOC species, therefore resulting in a large number of surrogate VOC classes for which emissions data were not available. Because of these difficulties, it was decided that more detailed sensitivity analyses of the remaining mechanisms was a more efficient use of resources than the effort required to obtain, implement, and test the Atkinson, Lloyd, Winges mechanism.

All three of the mechanisms reviewed in detail in this section are limited to a certain degree in their ability to simulate nighttime atmospheric chemical reactions. Many times, equilibrium assumptions are made regarding certain photochemical reactions. These assumptions, while valid during daytime periods, are not valid at night when no photochemical activity occurs. Because of the potential problem associated with use of chemical mechanisms for nighttime simulation, detailed analysis of each mechanism should be performed prior to use in nocturnal simulations.

One such analysis has been performed for the CBM-III mechanism. Dr. Jeffries of the University of North Carolina has supplied Radian with a modified CBM-III mechanism for use in the STRATOS model validation program (Eltgroth and Sedenberg, 1983b). For the CBM-III mechanism, the modification consisted of replacing the $NO_2 + NO_3$ reaction with three reactions to allow nocturnal non-photolytic removal of NO_3.

4.2 Description of Mechanisms

The three mechanisms selected for evaluation, CBM-III, CIT, and Demerjian, are briefly described below. More detailed discussions of the mechanisms are contained in the references cited above and elsewhere (Jeffries *et al*, 1981; McRae *et al*, 1984). A listing of each mechanism, with methanol chemistry added, is included in Appendix A. These listings of each mechanism are in the format for input into the Radian GCKM photochemical model.

4.2.1 Carbon Bond III

The Carbon Bond-III (CBM-III) mechanism is a lumped structure mechanism developed by SAI, Inc. A recent version of the EPA EKMA/OZIPP model, EKMA/OZIPM-2, uses the CBM-III mechanism. This EPA version of the CBM-III mechanism, which consists of 76 reactions, was used in the present study.

VOC species in the atmosphere, or in an emissions inventory, are assigned to each bond class in the mechanism according to their molecular structure. The bond classes in CBM-III are:

Paraffin (PAR) - single-bonded carbon atoms such as those in alkane compounds

Olefin (OLE) - terminally double-bonded carbon atoms such as those in the alkene compounds

Ethylene (ETH) - slowly reactive double-bonded carbon atoms, primarily consisting of ethylene

Aromatic (ARO) - reactive aromatic rings

Carbonyl (CARB) - carbonyl compounds such as those in the aldehydes and ketones and olefin compounds with internal double bonds

Dicarbonyl (DCRB) - highly photolytic, dicarbonyl compounds; these are primarily intermediate species which are not usually treated as inputs to the mechanism

Because CBM-III is based on bond structure, a single hydrocarbon species may be assigned to more than one of the above classes. For example, butene contains one double bond and two single bonds. Therefore, one mole of butene contains one mole of OLE bond and two moles of PAR bond.

4.2.2 CIT

The CIT mechanism, contained in the CIT Airshed Model, consists of 53 chemical reactions. The version used for this study was obtained from a recent study prepared for the EPA (McRae, et al, 1983). It is a lumped molecule mechanism consisting of the following surrogate VOC classes:

Alkane (ALK) - all alkanes

Olefin (OLE) - all alkenes except ethylene

Ethylene (ETH) - exclusively ethylene

Aromatic (ARO) - all compounds with reactive aromatic rings

Formaldehyde (HCHO) - exclusively formaldehyde

Higher Aldehydes (RCHO) - aldehydes other than formaldehyde

In the CIT mechanism, each hydrocarbon compound is assigned to one of the molecular classes according to the definitions above. Thus, for all compounds, other than ethylene and formaldehyde which are treated explicitly, the mechanism does not recognize any functional differences among different compounds in the same class. For example, xylene, ethylbenzene, and toluene are all placed in the aromatic class, and the carbon groups atached to the aromatic ring are not treated separately.

4.2.3 Demerjian

The Demerjian mechanism is contained in the Photochemical Box Model developed for EPA. A User's guide for this model is availabale (Schere and Demerjian, 1984). The most up-to-date version of the Demerjian mechanism was used for this study. In its present state, the mechanism consists of 61 reactions compared to 37 in the original version.

This mechanism is a lumped molecular mechanism consisting of the following VOC classes:

Paraffin (PAR) - all paraffinic (alkane) compounds

Olefin (OLE) - all alkenes except ethylene

Ethylene (ETH) - exclusively ethylene

Aromatic (ARO) - all compounds with reactive aromatic rings except toluene

Toluene (TOL) - exclusively toluene

Formaldehyde (HCHO) - exclusively formaldehyde

Higher Aldehydes (ALD) - aldehydes other than formaldehyde

The comments included in the description of the CIT mechanism also apply to the Demerjian mechanism, with the exception that Demerjian treats toluene separately from other aromatics.

4.3 Implementation of Chemical Mechanisms in GCKM

Each of the three mechanisms was obtained from the sources previously identified and adapted for input to Radian's General Chemical Kinetics Model (GCKM). Methanol chemistry was then added to each mechanism. Correct implementation of the CBM-III and Demerjian mechanisms was verified by executing the GCKM model with a test case obtained with each mechanism. The important details of this procedure are described below.

4.3.1 GCKM Treatment of Chemistry

A discussion of GCKM's treatment of chemical mechanisms is included in Appendix A. An important feature of GCKM is its ability to calculate the NO_2 photolysis rate for clear sky conditions as a function of day of year, time of day, and geographic location, if these parameters are input to the model. Schedules of ultraviolet radiation (UV), total solar radiation (TSR), temperature (T), and water vapor concentration (W) can also be input to the model. Reaction rates for any reaction in a mechanism can then be calculated from these inputs with one of the two following equations:

$$K = k_1 \text{ (UV, NO}_2\text{ photolysis rate, or TSR)}^{k_2} \qquad (4\text{-}1)$$

$$K = k_1 \exp (k_2/T) \qquad (4\text{-}2)$$

The values of k_1 and k_2 and the dependence (UV, NO_2 rate, TSR, or T) must be included as part of each reaction in the mechanism input to the model. If a water dependency (W) is specified, the model multiplies the reaction rate by the water vapor concentration.

4.3.2 CBM-III

The CBM-III mechanism included in the EKMA/OZIPM-2 model (Gipson, 1984) was input to GCKM. The mechanism contains seven photolytic reactions and several reactions whose rates have a temperature dependency identical to that in equation 4-2. As discussed in Section 4.3.1, GCKM includes an algorithm for this type of temperature dependency. The rates for the photolytic reactions are calculated internally by EKMA/OZIPM-2. The EPA Guideline for Using the Carbon Bond Mechanism in City-Specific EKMA (Gipson, 1984) contains a benchmark OZIPM-2 run using CBM-III. The reaction rates (k) for each photolytic reaction for each hour of the day from 8:00 a.m. to 6:00 p.m. are included.

For each photolytic reaction, a linear regression analysis was performed using lnK and ln (NO_2 photolysis rate) in the following relationship:

$$\ln K = \ln k_1 + k_2 \ln \text{ (NO}_2\text{ photolysis rate)} \qquad (4\text{-}3)$$

Equation 4-3 is a transformation of equation 4-1 obtained by taking the natural logrithm of both sides of the equation.

A correlation coefficient of 1.00 was obtained for the regression analysis for each reaction. This result indicates that equation 4-1 in Section 4.3.1 can be used to calculate the rate (K) of each photolytic reaction from the NO_2 photolysis rate. Therefore k_1 and k_2, computed in the regression analysis, were used in GCKM to compute reaction rates for each photolytic reaction. The maximum difference between a GCKM computed rate constant and the EPA benchmark case rate constant for any one hour was 6.9 percent. For most hours, the difference was less than 2.0 percent.

The GCKM model was then executed with the benchmark inputs for EKMA/OZIPM-2. The ozone concentrations calculated by GCKM are compared to those calculated by EKMA/OZIPM-2 in Table 4-1. Agreement between the two models is within 11% for all hours. The difference in computed maximum ozone concentration is due to the slight differences in the photolytic rate constants between the EPA and GCKM model runs.

4.3.3 CIT

The CIT mechanism used for this study was obtained from a recent report prepared for EPA (McRae et al, 1983). This version was determined to be the most up-to-date version available (Sienfeld, 1984). The mechanism contains seven photolytic reactions in addition to NO_2 photolysis. The photolyic reactions are calculated as a constant factor of the NO_2 photolysis rate, which can be readily accommodated by GCKM.

Two types of temperature dependencies are found in the CIT mechanism. Most are of the form of equation 4-2 in Section 4.3.1. The remainder are of the form:

$$K = A \times T^{B} \times \exp(-C/T) \qquad (4-4)$$

For these reactions, a constant temperature of 289°K was assumed for the first appearance of "T" in equation 4-4, simplifying the equation to be identical to equation 4-2. Because of the relatively small diurnal fluctuations in ambient temperature and the small values of "B" in the CIT mechanism, this simplification does not introduce a significant error.

TABLE 4-1. COMPARISON OF OZONE CONCENTRATIONS (PPM) USING CBM-III MECHANISM

Hour	GCKM	OZIPM-2
0800	0.00	0.00
0900	0.012	0.012
1000	0.045	0.047
1100	0.11	0.11
1200	0.19	0.20
1300	0.27	0.28
1400	0.30	0.31
1500	0.30	0.33
1600	0.31	0.34
1700	0.31	0.35
1800	0.32	0.36

A test case for the CIT mechanism could not be obtained from the developers. Therefore, as an alternative, the benchmark case used for CBM-III was also used to test the CIT mechanism. This was done by converting carbon bond rates to molecular class rates for all input NMOC concentrations. The CBM-III rather than the Dimerjian mechanism test case was used because the Demerjian test case assumed constant photolysis rates while the CBM-III case used typical time-varying photolysis rates.

Because this procedure involves some assumptions, the conversion is only an approximation. Also, because the mechanisms are different, identical inputs will not necessarily result in the prediction of identical ozone concentrations. Likewise, good agreement between the two mechanisms does not necessarily mean the mechanism is encoded properly. Nevertheless, the results of the comparison are presented in Table 4-2. A peak ozone concentration of 0.35 is predicted by CIT compared to 0.36 by EKMA/OZIPM-2. This represents an agreement within 3%. However, there are significant differences in predicted ozone concentration early in the simulation.

4.3.4 Demerjian

A copy of the Demerjian mechanism and a test run were obtained from Schere (Schere, 1984). The mechanism contains eleven photolytic reactions, whose rates are internally calculated by the Photochemical Box Model. The same linear regression procedure described for the CBM-III mechanism was used to calculate photolytic reaction rates from the NO_2 photolysis rates. Temperature-dependent reaction rates were either of the form in equation 4-2 of Section 4.3.1 or complex three-body calculations. For the three-body temperature dependencies, the reaction rate at a temperature of 298°K was used, thus introducing a slight deviation from the developer's version of the mechanism.

Table 4-3 a compares the ozone values calculated by GCKM and those calculated by the Photochemical Box Model. Although the time intervals are not identical for the two cases, agreement is within 2% when concentrations exceed 0.1 ppm. The test case used, however, assumed constant photolytic rate

TABLE 4-2. COMPARISON OF OZONE CONCENTRATION (PPM) CALCULATED BY CIT MECHANISM WITH OZIPM-2

Hour	CIT (GCKM)	CBM-III (OZIPM-2)
0800	0.00	0.00
0900	0.079	0.012
1000	0.033	0.047
1100	0.079	0.11
1200	0.13	0.20
1300	0.18	0.28
1400	0.23	0.31
1500	0.28	0.33
1600	0.32	0.34
1700	0.34	0.35
1800	0.35	0.36

TABLE 4-3. BENCHMARK RUN COMPARISON OF OZONE CONCENTRATION (PPM) USING DEMERJIAN MECHANISM

GCKM		Photochemical Box Model	
Time (min)	Ozone	Time (min)	Ozone
20	0.013	22.7	0.014
40	0.023	42.7	0.025
60	0.039	62.7	0.041
80	0.063	82.7	0.066
100	0.097	102.7	0.10
120	0.14	122.7	0.14
140	0.18	142.7	0.18
160	0.23	162.7	0.23
180	0.27	182.7	0.27
200	0.31	202.7	0.31
220	0.35	222.7	0.35
240	0.40	242.7	0.40
260	0.44	262.7	0.44
280	0.49	282.7	0.48
300	0.54	302.7	0.53
320	0.58	322.7	0.58
340	0.62	342.7	0.62
360	0.65	362.7	0.65
380	0.65	377.7	0.65

constants for all photolytic reactions. A test case with time-varying photolytic rate constants was not obtained.

4.3.5 Addition of Methanol Chemistry to the Reaction Mechanisms

After each mechanism was tested and determined to be satisfactorily encoded for input to GCKM, additional reactions to simulate methanol chemistry were added. As discussed in Section 2.0, methanol chemistry can be represented by the single reaction:

$$CH_3OH + OH \longrightarrow HO_2 + HCHO \tag{4-5}$$

The reaction has a well agreed upon rate of about 1500 ppm^{-1} min^{-1} (Dodge, 1984; SAI, 1983; CIT, 1983). Reaction 4-5 was added to each of the three mechanisms.

In the CIT and Demerjian mechanisms, HCHO chemistry is treated explicitly. Therefore, no other changes were required. In CBM-III, HCHO is included in the CARB group. Because the HCHO fraction becomes significant, if not dominant, with a methanol-fueled vehicle fleet, it is desirable to treat HCHO explicitly in the mechanism. Therefore, the following reactions were also added to the CBM-III mechanism:

$$HCHO + OH \longrightarrow HO_2 + CO \tag{4-6}$$

$$HCHO \xrightarrow{h\nu} 2HO_2 + CO \tag{4-7}$$

$$HCHO \xrightarrow{h\nu} H_2 + CO \tag{4-8}$$

The rates used by SAI for these reactions in their methanol photochemistry study were obtained from Whitten (1984). For reaction 4-6, the rate is 15,000 ppm^{-1} min^{-1}. For reaction 4-7, the rate is 0.00271 x (NO_2 photolysis rate). And for reaction 4-8, the rate is 0.00376 x (NO_2 photolysis rate). Although these same reactions are contained in the CIT and Demerjian mechanisms, the rate constants are somewhat different in each mechanism. At higher formaldehyde concentrations, the differences in rate constants (up to a factor of two) for these reactions may have a significant effect on the peak ozone predicted by each mechanism. For example, the CIT mechanism uses a rate of 0.00113 x (NO_2 photolysis rate) for reaction 4-7 (McRae et al., 1983), which is less than half the above rate used by SAI.

In the SAI methanol photochemistry study, methyl nitrite ($MeNO_2$) was identified as a species which may be introduced into the atmosphere in significant quantities with the conversion to methanol fueled vehicles (SAI, 1983). Because methyl nitrite is highly photolytic, the SAI researchers chose to include its chemistry in their mechanism by adding the following reactions:

$$MeNO_2 \rightleftharpoons CH_3O + NO \qquad (4\text{-}9)$$

$$CH_3O \longrightarrow HCHO + HO_2 \qquad (4\text{-}10)$$

The rate for the forward reaction 4-9 is 0.3 x (NO_2 photolysis rate), and the back reaction has a rate of 4.4×10^4 ppm^{-1} min^{-1}. Reaction 4-10 has a rate of 1.88 min^{-1}. These reactions were added to all three mechanisms in the present study. The reaction rates are those used by SAI (Whitten, 1984).

4.4 References for Section 4.0

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5.0 MODELING SENSITIVITY ANALYSIS

According to previous studies (SAI, 1983; CIT, 1983), it appears that methanol used as a fuel produces less ozone than petroleum-based fuels. However, before a complete assessment can be made of the change in ozone formation that would result from a significant conversion to methanol fuels, the sensitivity of each chemical mechanism to various input parameters must be established.

This section describes the results of 24 computer modeling sensitivity runs performed using Radian Corporation's General Chemical Kinetic Model (GCKM) and three atmospheric chemistry reaction mechanisms; the Carbon Bond III mechanism (CBM-III), the California Institute of Technology mechanism (CIT), and the Demerjian mechanism (Demerjian). The mechanisms have been modified as described in Section 4.0 to include identical methanol chemical reactions. Each mechanism does, however, handle non-methane organic compounds (NMOC) differently. The purpose of this modeling study is to assess the sensitivity of photochemical ozone formation to methanol emission, for the methanol-adapted CBM-III, CIT, and Demerjian mechanisms.

To present the results of the sensitivity analysis, this section is organized in the following manner. First, a brief discussion of the model used and the preparation of the input data is presented. Next, the base case modeling results for each mechanism are discussed. Third, the model sensitivity to the ratio of gasoline powered vehicles to methanol powered vehicles in the motor vehicle fleet is discussed. The HCHO/$MeNO_2$ ratio of methanol emissions is discussed fourth. Finally, a discussion of the relationship of surface and aloft ozone concentrations to ozone formation is presented.

5.1 Brief Description of Model Used

The Radian GCKM/TRAJ dispersion model was used to perform the modeling sensitivity study discussed in this section. This model is the same model discussed in Section 3.4.5. However, the trajectory option of GCKM/TRAJ was not used and so the model will be called simply GCKM for clarity in the remainder of this section.

The GCKM model can be operated in one of three modes. The mode discussed in Section 3.4.5 is the Atmospheric mode in which horizontal diffusion of the air parcel is simulated, air parcel trajectories are computed using METMOD, and emissions occur into the parcel explicitly. A second mode of GCKM allows simulation of smog chamber results. The third mode, used in this analysis, is called the EKMA mode and closely duplicates the EPA OZIPM-2 model.

In the EKMA mode of GCKM, horizontal diffusion of the air parcel is not simulated. Emissions are accounted for as emission fractions, or the addition of precursor pollutant concentrations to the air parcel as a fraction of the initial parcel concentration. Straight line trajectories are assumed, and so trajectories are not computed.

A single well mixed column of air is assumed to extend from the ground up to the top of the mixed layer. The mixed layer is allowed to expand vertically during the day as the mixing height rises. Concentration gradients at the edge of the well-mixed air column are assumed to be negligible so that horizontal diffusion can be ignored.

A more complete description of the GCKM/TRAJ model is given in the model User's Guide (Balentine, et al, 1984).

5.2 Input Data Preparation

The first step in this sensitivity analysis was to establish a reasonable data base for use in modeling. This data base defined the atmospheric conditions, initial, surface, and aloft species concentrations, and most importantly, the quantity of reactive emissions. This section will discuss the basis for the choices of each of these model inputs.

5.2.1 Atmospheric Conditions

The model inputs for all GCKM simulations are based on the atmospheric conditions of June 27, 1974, for Los Angeles, California. There are two reasons for selecting this date. First, monitoring data have shown that ozone concentrations were elevated on June 27, 1974, (EPA, 1977; SAI, 1983). Second, previous ozone modeling studies have predicted elevated ozone concentrations when June 27, 1974 atmospheric conditions were modeled (SAI, 1983, EPA, 1977). Therefore, for consistency and comparability of modeling results, all GCKM simulations were performed for the Los Angeles, California, area with June 27, 1974, atmospheric conditions. Since ozone formation is a function of sunlight, all GCKM model runs simulated the 10-hour period between 0800 hours and 1800 hours.

Atmospheric conditions such as hourly temperature and mixing height variation also affect ozone formation. Table 5-1 lists the temperature and mixing height GCKM input values for all model simulations.

5.2.2 Initial, Air Parcel and Aloft Precursor Concentrations

The selection of reasonable initial concentrations of ozone precursors in the air parcel and above the mixing height is very important in an ozone formation sensitivity analysis. For this analysis, 0.5 ppm NMOC, 0.064 ppm NO_x, and 0.06 ppm O_3 were selected as the GCKM inputs for the initial air parcel concentrations. These values are typical concentrations for Los Angeles (EPA, 1981). The initial parcel concentration was assumed to consist of a background surface concentration and a concenration due to emissions from manmade sources.

The NMOC initial concentration was speciated for each reaction mechanism and held constant at 0.5 ppmC throughout the analysis. An example of the calculation method used to allocate the initial concentration among each species class is shown in Appendix B. The NO_x concentration was split as 75 percent NO and 25 percent NO_2 (on a molar basis). This NO_x ratio was constant for each mechanism.

TABLE 5-1. HOURLY TEMPERATURE AND MIXING HEIGHT SCHEDULES USED FOR ALL MODEL RUNS

Time (hrs)	Temperature (°C)	Mixing Height (m)
0800	23.9	70.1
0900	26.8	116.2
1000	29.9	156.3
1100	32.1	300.7
1200	33.7	356.9
1300	36.0	447.6
1400	37.5	528.4
1500	38.6	539.1
1600	36.6	523.9
1700	29.3	520.0
1800	26.7	520.0

(Source: SAI, 1983)
Note: Values representative of Los Angeles for June 27, 1974.

Aloft concentrations for NMOC, NO_x, and O_3 were selected from typical values for the Los Angeles area reported by Systems Applications, Inc. (SAI, 1983). Both NMOC and NO_x aloft concentrations were speciated by the same methods described for the initial concentrations. The typical Los Angeles area aloft O_3 concentration selected for input to GCKM was 0.08 ppm.

Table 5-2 lists the initial surface and aloft concentrations, by species, for each mechanism. Tables 5-2 through 5-5 present the NMOC initial species concentrations by mechanism for each case modeled.

5.2.3 Non-Methane Organic Compound Emissions

The projected Los Angeles, California, 1987 CBM-III emission inventory presented by SAI was chosen as the emissions basis for all GCKM simulations. Table 5-6 shows the NMOC and NO_x emissions from this inventory. Total NMOC emitted was assumed to be constant for all scenarios and for each mechanism. Hourly emissions were calculated by dividing the daily emission totals by 24 and assuming a constant rate for the ten-hour simulation. These hourly emissions were then input to GCKM as fractions of the air parcel initial concentrations using the same methodology used for the OZIPM-2 model. Because the parcel initial concentration was held constant for each scenario and the initial concentration was assumed to be caused by emissions, constant emission fractions were used for each scenario for each mechanism. The calculation of the emission fraction used for each run is given in Appendix B.

5.3 Sensitivity Study Results

Twenty-four model sensitivity runs were performed using the CBM-III, CIT, and Demerjian mechanisms. The runs consisted of a simulation for each mechanism for each of the eight modeling scenarios. Brief descriptions of these scenarios and the resulting peak ozone concentrations, predicted for the scenarios, are given in Table 5-7. Peak ozone concentration differences between scenarios, for a given mechanism, were generally small. The exception is for the CIT mechanism which predicted very significant differences in peak ozone concentrations between scenarios.

TABLE 5-2. MODEL INPUT OZONE PRECURSOR CONCENTRATIONS

Species	Initial	Aloft
All Mechanisms		
NO_x	0.060	0.003
NO	0.045[a]	0.002[a]
NO_2	0.015	0.001
O_3	0.06[b]	0.08[c]
CO	2.0	0
H_2O_2	1.0E-6	0
CBM-III Mechanism		
PAR	d	0.0916
ETH	d	0.0021
OLE	d	0.0003
ARO	d	0.0011
CARB	d	0.0289
CIT Mechanism		
OLE	d	0.0005
ALK	d	0.019
ARO	d	0.013
ETH	d	0.0022
RCHO	d	0.0077
HCHO	d	0.011
Demerjian Mechanism		
OLE	d	0.0005
PAR	d	0.019
ETH	d	0.0022
ALD	d	0.0077
ARO	d	0.0008
TOL	d	0.0005
HCHO	d	0.011

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[a] Based on assumption of total NO_x split of 75% NO, 25% NO_2 per EPA, 1981.

[b] Decreased to 0.03 ppm for O_3 aloft sensitivity case.

[c] Decreased to 0.04 ppm for O_3 aloft sensitivity case.

[d] Based on emissions per SAI, 1983. Varies for each sensitivity case. See Tables 5-4 through 5-6.

TABLE 5-3. CBM-III REACTION MECHANISM INITIAL NMOC SPECIES CONCENTRATIONS IN AIR PARCEL (PPM)

Species	Base Case	50% Methanol Vehicles Case	100% Methanol Vehicles Cases 10% HCHO 1% $MeNO_2$	100% Methanol Vehicles Cases 10% HCHO 5% $MeNO_2$	100% Methanol Vehicles Cases 20% HCHO 5% $MeNO_2$	100% Methanol Vehicles Cases 20% HCHO 1% $MeNO_2$
PAR	0.3625	0.2848	0.2071	0.2071	0.2071	0.2071
ETH	0.0160	0.0114	0.0072	0.0072	0.0072	0.0072
OLE	0.0130	0.0084	0.0041	0.0041	0.0041	0.0041
ARO	0.0105	0.0077	0.0049	0.0049	0.0049	0.0049
CARB	0.0180	0.0144	0.0111	0.0110	0.0110	0.0110
CH_3OH	0	0.1025	0.2050	0.1958	0.1728	0.1820
HCHO	0	0.0115	0.0231	0.0231	0.0461	0.0461
$MeNO_2$	0	0.0011	0.0023	0.0115	0.0115	0.0023

Note: Species concentrations are based on 0.5 ppmC selected as a typical 6-9 a.m. NMOC concentration for Los Angeles, California (SAI, 1983). Percents are based on moles of NMOC.

TABLE 5-4. CIT REACTION MECHANISM INITIAL NMOC SPECIES CONCENTRATIONS IN AIR PARCEL (PPM)

			100% Methanol Vehicles Cases			
Species	Base Case	50% Methanol Vehicles Case	10% HCHO 1% $MeNO_3$	10% HCHO 5% $MeNO_3$	20% HCHO 5% $MeNO_3$	20% HCHO 1% $MeNO_3$
ALK	0.0620	0.0508	0.0384	0.0384	0.0384	0.0384
ETH	0.0133	0.0098	0.0065	0.0065	0.0065	0.0065
OLE	0.0190	0.0121	0.0062	0.0062	0.0062	0.0062
ARO	0.0104	0.0076	0.0050	0.0050	0.0050	0.0050
RCHO	0.0038	0.0032	0.0025	0.0025	0.0025	0.0025
CH_3OH	0	0.1025	0.2050	0.1958	0.1728	0.1820
HCHO	0.0055	0.0162	0.0269	0.0269	0.0499	0.0499
$MeNO_3$	0	0.0011	0.0023	0.0115	0.0115	0.0023

Note: Species concentrations are based on 0.5 ppmC selected as a typical 6-9 a.m. NMOC concentration for Los Angeles, California (SAI, 1983). Percents are based on moles of NMOC.

TABLE 5-5. DEMERJIAN REACTION MECHANISM INITIAL NMOC SPECIES CONCENTRATIONS IN AIR PARCEL (PPM)

Species	Base Case	50% Methanol Vehicles Case	100% Methanol Vehicles Cases 10% HCHO 1% $MeNO_3$	10% HCHO 5% $MeNO_3$	20% HCHO 5% $MeNO_3$	20% HCHO 1% $MeNO_3$
PAR	0.0620	0.0508	0.0384	0.0384	0.0384	0.0384
ETH	0.0133	0.0098	0.0065	0.0065	0.0065	0.0065
OLE	0.0190	0.0121	0.0062	0.0062	0.0062	0.0062
ARO	0.0062	0.0046	0.0030	0.0030	0.0030	0.0030
TOL	0.0042	0.0030	0.0020	0.0030	0.0030	0.0030
ALD	0.0038	0.0032	0.0025	0.0025	0.0025	0.0025
CH_3OH	0	0.1025	0.2050	0.1958	0.1728	0.1820
HCHO	0.0055	0.0162	0.0269	0.0269	0.0499	0.0499
$MeNO_3$	0	0.0110	0.0023	0.0115	0.0115	0.0023

Note: Species concentrations are based on 0.5 ppmC selected as a typical 6-9 a.m. NMOC concentration for Los Angeles, California (SAI, 1983). Percents are based on moles of NMOC.

TABLE 5-6. LOS ANGELES 1987 PROJECTED MOBILE AND OTHER SOURCE EMISSIONS

	Emissions (g-moles/day)		
	Motor Vehicles	All Other Sources	Totals
NMOC (as carbon)	90,600	106,000	196,000
NO_x	39,700	22,100	61,800

(Source: SAI, 1983)

Note: All emissions are rounded to three significant figures.

TABLE 5-7. SUMMARY OF PEAK OZONE CONCENTRATION FOR EACH SCENARIO AS PREDICTED BY EACH MECHANISM

	Scenario Description							
	Emissions from Methanol-Fueled Vehicles (% of Total)			Initial Concentrations (ppm)		Predicted Peak Ozone Concentration (ppm)		
Scenario Title	CH_3OH	HCHO	$MeNO_2$	O_3 Surface	O_3 Aloft	CBM-III	CIT	Demerjian
Base Case	0	0	0	0.06	0.08	0.26	0.20	0.32
50% Methanol Vehicles Case	89	10	1	0.06	0.08	0.25	0.28	0.30
100% Methanol Vehicles Case	89	10	1	0.06	0.08	0.24	0.17	0.29
Ozone Aloft Sensitivity Case, 100% Methanol Vehicles	89	10	1	0.06	0.04	0.22	0.14	0.28
Surface Ozone Sensitivity Case, 100% Methanol Vehicles	89	10	1	0.03	0.04	0.22	0.13	0.27
Formaldehyde/Methyl Nitrite Case (10%/5%)	85	10	5	0.06	0.08	0.25	0.18	0.30
Formaldehyde/Methyl Nitrite Case (20%/1%)	79	20	1	0.06	0.08	0.25	0.19	0.30
Formaldehyde/Methyl Nitrite Case (20%/5%)	75	20	5	0.06	0.08	0.25	0.20	0.30

Plots of the concentrations of primary species (NO, NO_2, O_3, PAN, and NMOC) versus time for each sensitivity run are given in Appendix C. Detailed discussions of each scenario and the modeling results are given in the remainder of this section. Listings of the predicted species concentrations for each time step for all sensitivity runs are given in Appendix D.

5.3.1 Base Case Scenario

The base case model run was made for each of the three mechanisms. The base case was for June 27, 1974, with 1987 emission rates. All vehicles were assumed to be burning gasoline. No methanol chemistry was included in the mechanisms. The purpose of the base case was to establish a starting point from which input parameters could be varied and comparisons made.

The model inputs for the base case have been presented in Section 5.2. Inputs were identical for the three mechanisms with the exception of the distribution of the NMOC species. These differences reflect the different lumping procedures used by each mechanism rather than a difference in the NMOC composition in the atmosphere. Total NMOC (as carbon) was held constant at 0.5 ppmC.

Figure 5-1 presents the base case ozone concentrations as a function of time for each of the three mechanisms. Peak ozone was reached at 600 minutes (6:00 PM LDT) with all three mechanisms. The Demerjian mechanism predicted a peak ozone concentration of 0.32 ppm, CBM-III predicted a peak of 0.26, and CIT predicted a peak of 0.20 ppm. Because the base case did not correspond to an observed ozone maximum (due primarily to use of projected 1987 emission rates), the modeled values can only be compared with each other. The mean ozone concentration predicted by the three mechanisms was 0.26 ppm, which is equal to the peak predicted by CBM-III. The Demerjian and CIT peaks were 23% above and 23% below the mean, respectively.

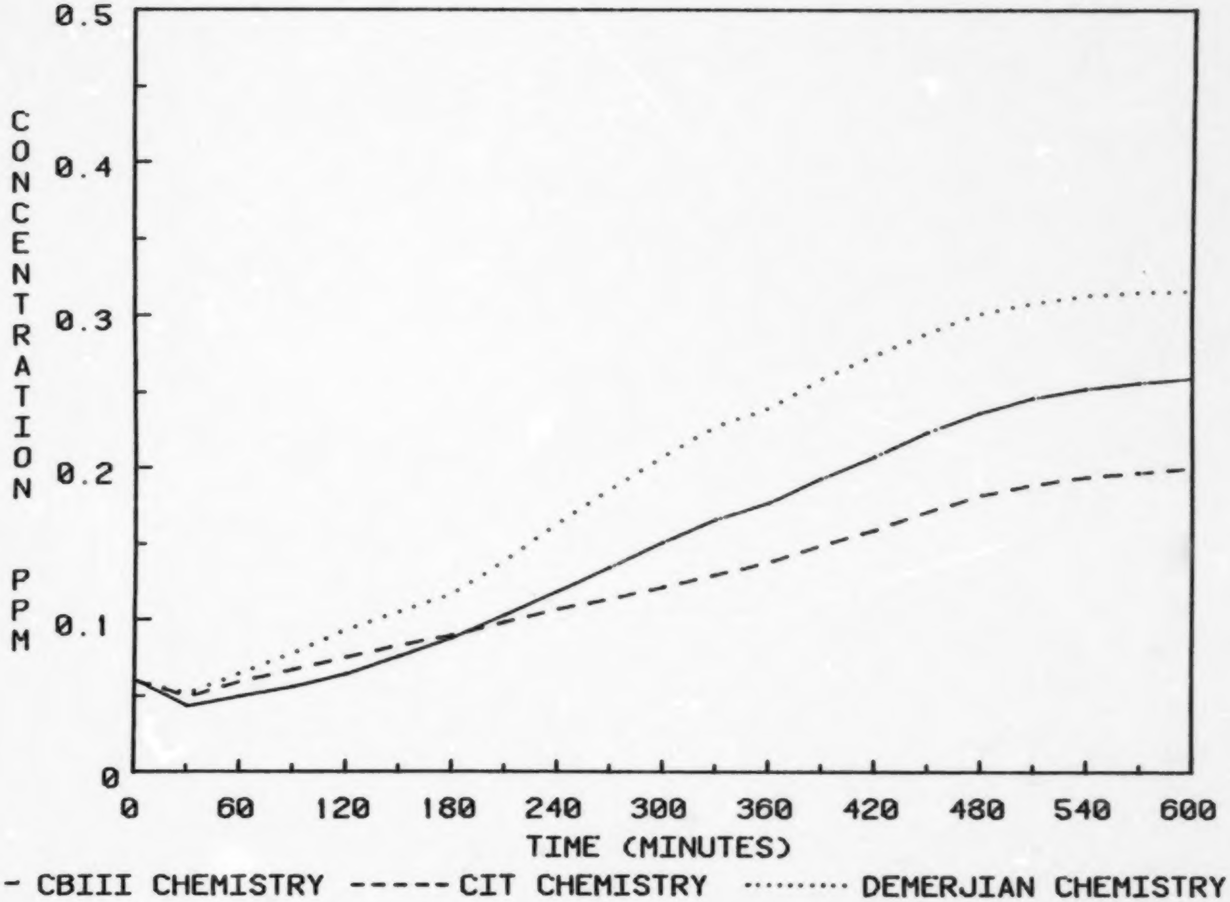


Figure 5-1. Predicted Ozone Concentrations for Base Case Scenario for Each Mechanism.

5.3.2 Fifty Percent Methanol Conversion Scenario

Each mechanism was run assuming that fifty percent of the vehicles in the Los Angeles area inventory were converted to methanol fuel. The emissions from the methanol-fueled vehicles were assumed to be 89% methanol (CH_3OH), 10% formaldehyde (HCHO), and 1% methyl nitrite ($MeNO_2$). The remaining NMOC was speciated according to the appropriate chemical reaction mechanism. All percentages are based on moles of NMOC. All other inputs, including initial NO_x, O_3, NMOC concentrations and emission fractions, were left unchanged from the base case. The initial NMOC species concentration resulting from this scenario have been presented in Tables 5-4 through 5-6 of Section 5.1.

Figure 5-2 presents the ozone concentrations as a function of time for each mechanism for the 50% conversion scenario. Compared with the base case, the Demerjian and CBM-III mechanisms predicted a slight decrease in peak ozone concentration (0.02 ppm and 0.01 ppm, respectively) with the 50% conversion to methanol vehicles. The CIT mechanism predicted an increase from 0.20 ppm to 0.28 ppm. This increase was due to a rapid rise in ozone concentration from 60 to 120 minutes into the simulation (9:00 AM to 10:00 AM). The increase in ozone coincided with a large increase in PAN, a large decrease in NO and NO_2, and a large increase in radical population (OH and HO_2) compared to the base case.

The behavior predicted by the CIT mechanism for the 50% conversion scenario is not consistent with the trends predicted by the other scenarios or by the CBM-III and Demerjian mechanisms. Both the ozone and PAN concentrations rise dramatically at 90 minutes into the simulation and peak at 120 minutes. The PAN concentration at 120 minutes is approximately two times higher than any other CIT run. A plot of the 50% case including ozone, PAN, NO, NO_2, and NMOC is given in Appendix C. Modeled 30-minute concentrations are given in Appendix D. Additional discussion of the CIT 50% conversion scenario is given in Appendix E.

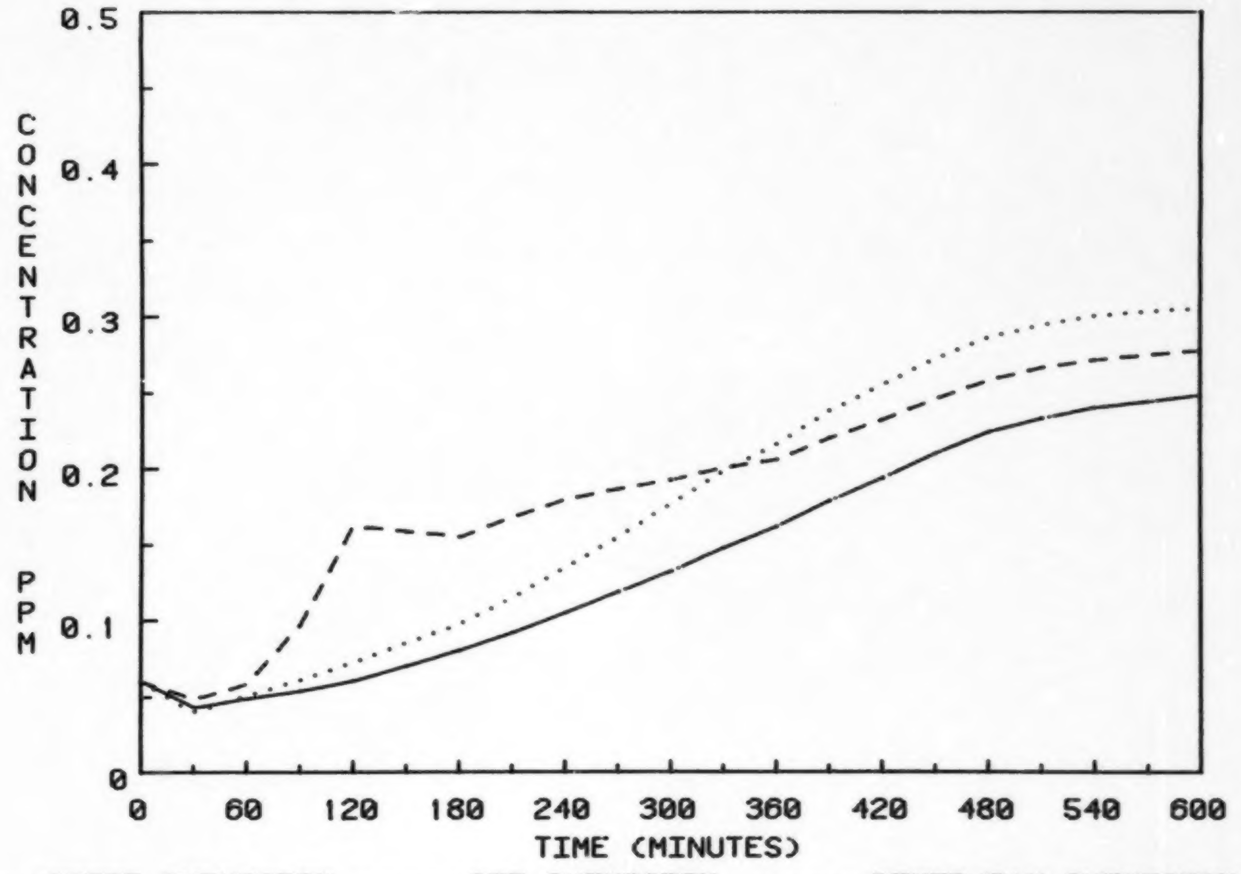


Figure 5-2. Predicted Ozone Concentrations for 50% Methanol Conversion Scenario for Each Mechanism.

The results of the 50% conversion scenario modeling seem to indicate that the mechanism is overly sensitive to changes in the NMOC species distribution. It should be noted that because we were unable to obtain an actual test case from the developers to verify the CIT mechanism, some uncertainty exists as to its correct implementation in this study. However, other researchers have also obtained poor results with the earlier versions of the CIT mechanism (Jeffries, et al, 1981).

The results of the 50% methanol conversion case and the problems with obtaining and implementing the CIT mechanism tend to make the mechanism less desirable for future studies compared to CBM-III and Demerjian. Additional analysis is needed to determine the source of the unusual results for the CIT mechanism for the 50% conversion scenario.

5.3.3 One Hundred Percent Methanol Conversion Scenario

Each mechanism was run assuming that 100% of the vehicles in the projected 1987 Los Angeles area inventory were converted to methanol fuel. The emissions from the methanol fueled vehicles were assumed to be 89% CH_3OH, 10% HCHO, and 1% $MeNO_2$. Non-vehicle NMOC emissions were speciated according to the appropriate chemical reaction mechanism for each GCKM run. All other inputs were the same as the base case.

Figure 5-3 presents the ozone concentrations as a function of time for each mechanism for the 100% conversion scenario. Compared with the base case, the CBM-III, CIT and Demerjian mechanisms predicted a decrease in peak ozone concentrations (0.02 ppm, 0.03 ppm and 0.03 ppm, respectively) with the 100% conversion to methanol vehicles.

Each mechanism appeared to be equally sensitive to methanol emissions when compared to the base case. The CBM-III and Demerjian mechanism each predictd a further decrease of 0.01 ppm in peak ozone when methanol conversion increases from 50% to 100%. The CIT mechanism results did not show a

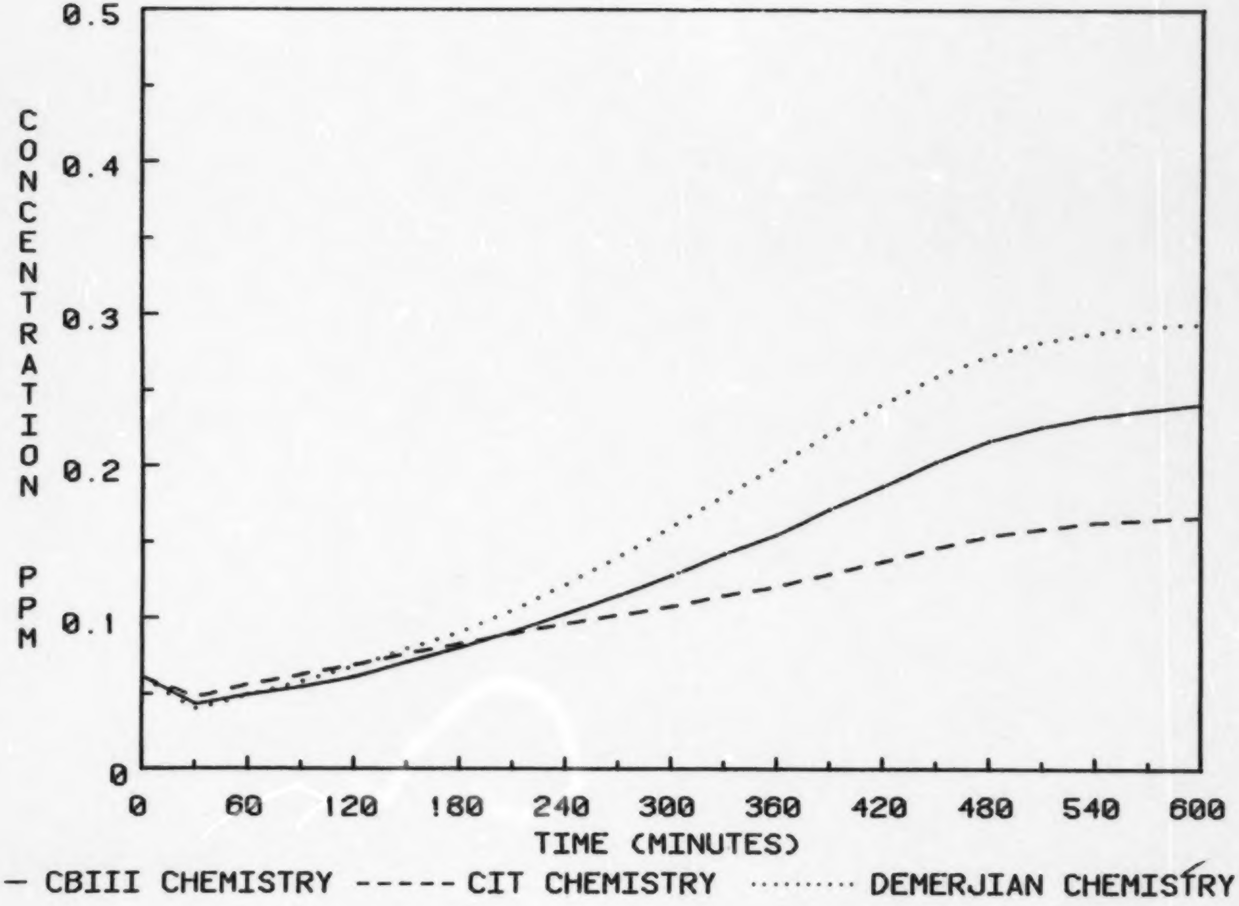


Figure 5-3. Predicted Ozone Concentrations for 100% Methanol Conversion Scenario for Each Mechanism.

continuation of the same behavior exhibited for the 50% conversion scenario. Thus, the CIT results for the 50% methanol conversion are not only inconsistent with the other two mechanisms, but also inconsistent with the CIT base case and 100% conversion results. This is clearly illustrated in Figure 5-4 which presents plots of the hourly ozone concentration predicted for each scenario for each of the three mechanisms. In CBM-III and Demerjian, the ozone concentration for the 50% case remains between the concentration for the base case and 100% case throughout the simulation. In CIT, the ozone concentration for the 50% case increases rapidly early in the simulation and remains elevated above the predicted ozone concentration for both the base case and the 100% case.

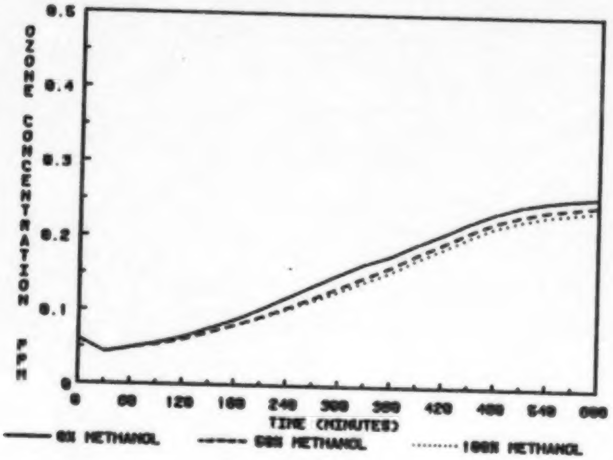
5.3.4 Ozone Background/Aloft Concentration Scenarios

Three ozone background/aloft concentration scenarios were examined for each chemical reaction mechanism for the 100% methanol conversion case. A surface ozone concentration of 0.06 ppm and an aloft ozone concentration of 0.08 ppm were used as the initial case. In each of the two remaining cases, the existing ozone concentration at the surface or aloft was varied. All other model inputs were the same as the base case for each reaction mechanism. The ozone sensitivity cases examined were:

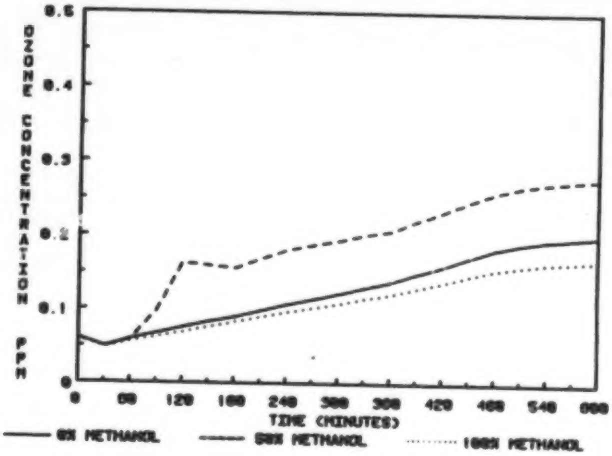
- Surface ozone concentration = 0.06 ppm
  Aloft ozone concentration = 0.08 ppm
- Surface ozone concentration = 0.06 ppm
  Aloft ozone concentration = 0.04 ppm
- Surface ozone concentration = 0.03 ppm
  Aloft ozone concentration = 0.04 ppm

The purpose of these cases was to examine the effect of existing surface and aloft ozone concentrations on the peak ozone values predicted by GCKM using the CBM-III, the CIT, or the Demerjian chemical reaction mechanisms.

A. Carbon Bond III Chemistry



B. CIT Chemistry



C. Demerjian Chemistry

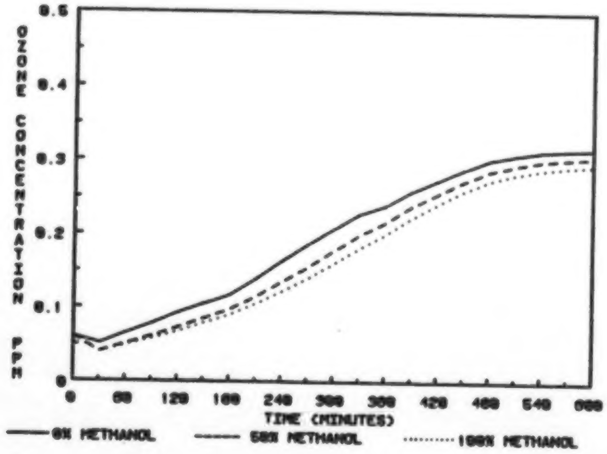


Figure 5-4. Predicted Ozone Concentrations for Methanol Substitution Scenarios for Each Mechanism.

Plots of the predicted ozone concentrations for each of the three ozone sensitivity cases are presented in Figure 5-5 for the CBM-III, CIT, and Demerjian mechanisms. These plots show that ozone formation by the CBM-III, CIT, and Demerjian reaction mechanisms was decreased by a decrease in either surface or aloft ozone concentrations. However, for the CBM-III and CIT mechanisms, the decrease in ozone formation was more related to a decrease in aloft ozone concentrations than surface ozone concentrations. For example, as aloft ozone concentration decreased from 0.08 ppm to 0.04 ppm, the CBM-III predicted ozone concentration decreased 0.02 ppm (from 0.24 ppm to 0.22 ppm). The same aloft ozone concentration decrease resulted in a 0.03 ppm (0.17 ppm to 0.14 ppm) reduction in peak ozone concentration for the CIT mechanism. Peak ozone based on the Demerjian mechanism decreased 0.01 ppm.

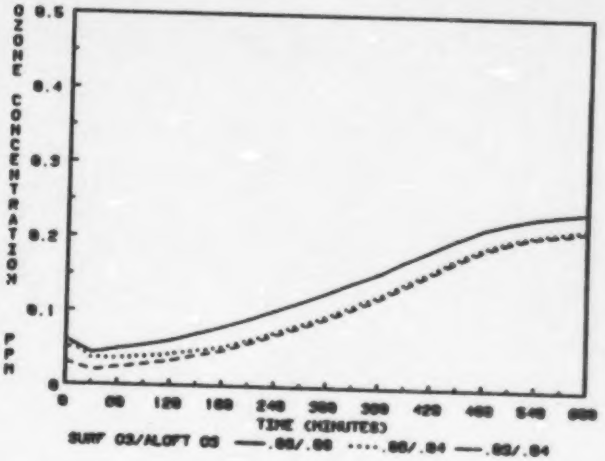
Surface ozone concentrations affected predicted peak ozone concentrations very little. For a surface ozone concentration reduction from 0.06 ppm to 0.03 ppm, the CBM-III peak ozone concentration remained 0.22 ppm. The CIT and Demerjian mechanism peak ozone concentrations are reduced by only 0.01 ppm (0.14 ppm to 0.13 ppm, and 0.28 ppm to 0.27 ppm, respectively). (See Table 5-7.)

Two conclusions can be drawn from this case. First, while the CBM-III and Demerjian mechanisms are sensitive to decreases in aloft ozone concentrations, the CIT reaction mechanism is the most sensitive chemical reaction mechanism to decreases in aloft ozone concentrations. Second, decreases in surface ozone concentrations do not significantly affect peak ozone concentrations for the CBM-III, the CIT, and the Demerjian chemical reaction mechanisms.

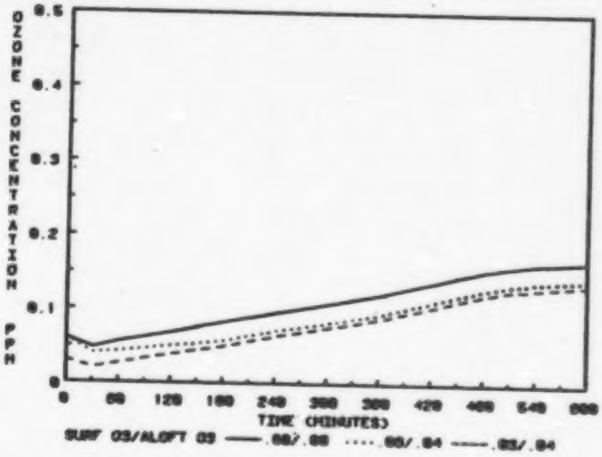
5.3.5 Formaldehyde/Methyl Nitrite Emission Fraction Scenarios

Four different HCHO/$MeNO_2$ emission ratios were examined for the 100% methanol conversion case. All other model inputs for these runs did not vary from the base case inputs. The CH_3OH, HCHO, $MeNO_2$ distributions examined were:

A. Carbon Bond III Chemistry



B. CIT Chemistry



C. Demerjian Chemistry

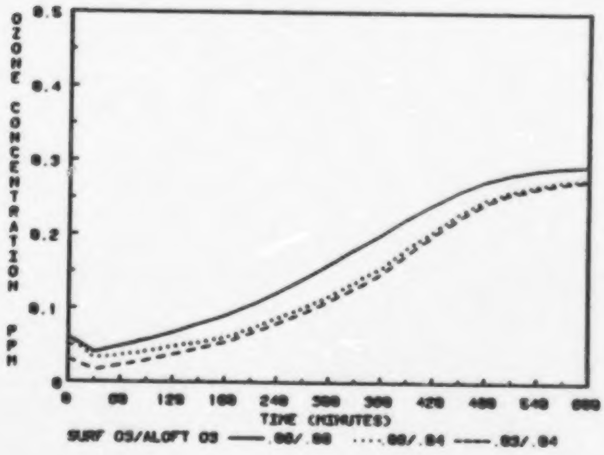


Figure 5-5. Predicted Ozone Concentration for Initial Ozone Concentration Scenarios for Each Mechanism.

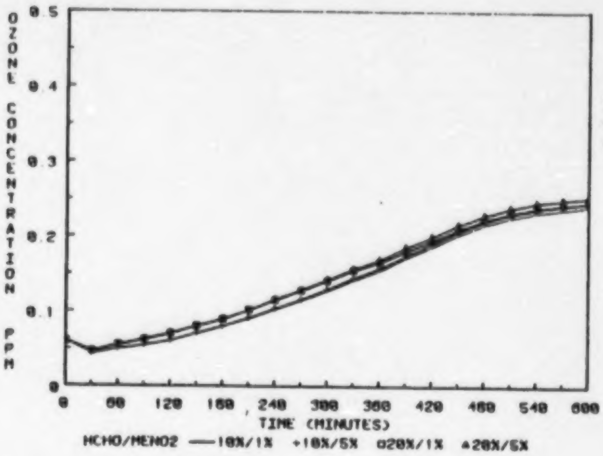
- 89% CH_3OH, 10% HCHO, 1% $MeNO_3$
- 85% CH_3OH, 10% HCHO, 5% $MeNO_3$
- 79% CH_3OH, 20% HCHO, 1% $MeNO_3$
- 75% CH_3OH, 20% HCHO, 5% $MeNO_3$

These HCHO/$MeNO_3$ emission rates were chosen based on information found in the literature (SAI, 1983). Systems Applications, Inc. indicated that the likely range of methanol conversion to formaldehyde is 0 to 20% of total methanol emissions. SAI also indicated that $MeNO_3$ emissions are 1 to 5% of the total methanol emissions. Again, as in all cases, total NMOC was held constant at 0.5 ppmC.

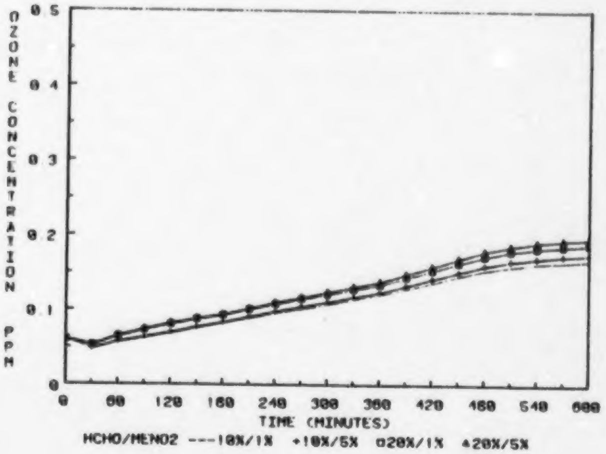
Plots of the predicted ozone concentrations for each of the four HCHO/$MeNO_3$ emission fraction sensitivity cases are presented in Figure 5-6 for the CBM-III, CIT, and Demerjian mechanisms. As the HCHO emissions were increased from 10% to 20% ($MeNO_3$ constant at 1%), peak ozone concentrations increased slightly for all chemical mechanisms (0.01 ppm for CBM-III, 0.02 ppm for CIT, and 0.01 for Demerjian). Also, the rate of hourly ozone production increased slightly for each mechanism. As $MeNO_3$ emissions (HCHO constant at 10%) were increased from 1% to 5% of methanol emissions only a slight increase in peak or hourly ozone concentration was observed (approximately 0.01 ppm for all reaction mechanisms). As the HCHO emissions increased from 10% to 20%, and the $MeNO_3$ emissions increased from 1% to 5% of methanol emissions, peak ozone concentrations increased 0.01 ppm for CBM-III and Demerjian. The CIT mechanism showed a 0.03 ppm increase in peak ozone concentrations.

In general, the CBM-III and Demerjian reaction mechanisms are only slightly sensitive to HCHO emissions from 10% to 20% of methanol emissions and $MeNO_3$ emissions from 1% to 5% of methanol emissions. Only the CIT mechanism shows a moderate sensitivity to increases in HCHO or $MeNO_3$ concentrations (a 0.03 ppm ozone increase).

A. Carbon Bond III Chemistry



B. CIT Chemistry



C. Demerjian Chemistry

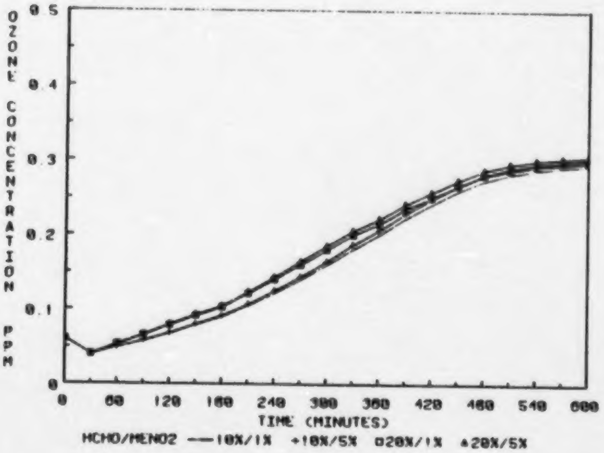


Figure 5-6. Predicted Ozone Concentrations for Formaldehyde/Methyl Nitrite Emission Scenarios for Each Mechanism.

5.4 References for Section 5.0

Balentine, H.W., Eltgroth, M.W., Smith, C., and Langevin, S.A. (1984): User's Manual for the General Chemical Kinetic Model with Trajectory Option (GCKM/TRAJ), DCN 84-244-005-04, Radian Corporation of Austin, Texas, September, 1984.

California Institute of Technology for Jet Propulsion Laboratory (1983): California Methanol Assessment: Volume II: Technical Report: Chapter 6: Air-Quality Impact of Methanol Use in Vehicles, Report for the California Energy Commission.

EPA (1977): Uses, Limitations and Technical Basis of Procedures for Quantifying Relationships Between Photochemical Oxidents and Precursors. EPA report EPA-450/2-77-021A, U.S. EPA, Research Triangle Park, NC.

Eltgroth, M.W. (1981): A General Chemical Kinetic Simulation Computer Program for Use with Multiple Reaction Mechanisms. Radian Corporation report.

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Hogo, H., G.Z. Whitten, and S.D. Reynolds (1981): Application of the Empirical Kinetic Modeling Approach (EKMA) to the Tulsa Area. Report to U.S. EPA by Systems Applications, Inc. under Contract No. 68-02-3376.

Jeffries, H.E., K.G. Sexton, and C.N. Salmi (1981): The Effects of Chemistry and Meteorology on Ozone Control Calculations Using Simple Trajectory Models and the EKMA Procedure. Report to U.S. EPA by the University of North Carolina under Contract No. 68-02-3523, EPA report No. EPA-450/4-81-034.

6.0 SUMMARY AND RECOMMENDATIONS

This section briefly summarizes Radian's recommendations. These recommendations cover the four major areas addressed respectively in Sections 2.0, 3.0, 4.0, and 5.0.

1. Methanol Chemistry and Emissions Summary
2. Recommended Dispersion Models
3. Recommended Mechanisms
4. Recommended Additional Analyses

6.1 Methanol Chemistry and Emissions Summary

One of the potential advantages of using methanol as a fuel is that it burns relatively clean and evaporative emissions are simple and comparatively unreactive. Compared to gasoline, burning methanol generally results in fewer combustion products. The main combustion products are unburned methanol, formaldehyde (HCHO, a partial combustion product), CO, NO_x, and smaller amounts of post-combustion combination products, perhaps the only one of importance being methyl nitrite.

The essential atmospheric chemistry of methanol is simple. Nearly all researchers agree (Dodge, 1984) that there is only one significant reaction and that is with the hydroxyl radical, OH:

$$CH_3OH + OH \longrightarrow HO_2 + HCHO \qquad (6\text{-}1)$$

Even the rate of this reaction is well agreed upon, and the inclusion of this reaction in any chemical reaction mechanism should be straightforward. Compared to most hydrocarbon species, the methanol is rather slow to react. The rate constant of methanol is about half that of butane. When methanol does react, as in equation 6-1, it generates radicals and formaldehyde. Therefore, it should not be considered (or lumped) as a general hydrocarbon but rather is best treated as a separate species. Since all mechanisms contain OH and HO_2 radicals, they should be able to assimilate the newly introduced methanol, formaldehyde, and methyl nitrite reactions.

As seen in equation 6-1, formaldehyde (HCHO) is one of the products of the atmospheric methanol reaction. Formaldehyde is photochemically active to ultraviolet light and generates radicals when it dissociates. It is an important source of radicals in most mechanisms. Essentially all atmospheric photochemical mechanisms take account of formaldehyde.

Methyl nitrite is not formed in the combustion chamber but in the exhaust of the engine. Emissions of methyl nitrite are proportional to the NO concentration in the exhaust, and hence the exhaust dilution.

The only fate of methyl nitrite in the mechanisms reviewed is photodissociation into radicals. That is, methyl nitrite can only be removed during daylight hours while there is sunlight to photodissociate the molecules. Consequently, substantial quantities of methyl nitrite would be expected to build up at night and result in another possible large source of radicals at first light. Formaldehyde also could have a similar fate. These methyl nitrite reaction products could therefore potentially have a significant influence on ozone formation on the second day and subsequent days of an ozone episode. However, very little is known about methyl nitrite chemistry in the atmosphere. Therefore, smog chamber studies should be conducted to evaluate speculations regarding its fate.

The number, and possibly the mixture, of hydrocarbons emissions may change with substantial use of methanol fuel. Any chemistry mechanisms used to simulate methanol photochemistry should be validated over the expected ranges of NMOC concentrations and types of mixtures. Also, with lower NO_x emissions expected, the model should be validated in the lower NO_x ranges. Since many models are sensitive to NMOC/NO_x ratios, caution should be exercised when comparing results if the NMOC/NO_x ratios are different. However, if both NMOC and NO_x are expected to be reduced or unchanged, the NMOC/NO_x ratio may not vary drastically.

6.2 Recommended Dispersion Models

No one model is recommended for use in all cases. The models reviewed have been recommended in an order reflecting data coverage. Some models have been eliminated because of difficulties in having the model change its chemical reaction mechanism or other basic problems.

For simulations in the Los Angeles area the recommended models, in order of preference, are:

1. SAI Urban Airshed
2. Level II EKMA using OZIPM-2
3. MARC-1

Each of these models should be capable of being used for Los Angeles. The first two models have been used in previous (and current) modeling studies for Los Angeles. The MARC-1 model is included as an alternative Eulerian model.

For simulations outside of Los Angeles the recommended models are:

- Urban Airshed Model
- STRATOS
- OZIPM-2
- GCKM/TRAJ

The selection of the model to use is determined by the amount of data coverage available and the type of analysis to be performed. The user should select the model for which the appropriate amount of data is available.

6.3 Recommended Mechanisms

The CBM-III and Demerjian chemical kinetic mechanisms are recommended for use in future assessments of the impact of methanol fuel conversion on ozone photochemistry.

Both the CBM-III and Demerjian mechanisms predicted similar ozone concentrations for the limited set of scenarios modeled. No significant difference in each mechanism's simulation of ozone photochemistry was noted.

The limited set of sensitivity runs performed for this study is not sufficient to allow one mechanism to be recommended over the other. However, two additional factors need to be considered when selecting a mechanism.

First, the size of the mechanism should be considered. The Demerjian mechanism has fewer reactions than does the CBM-III mechanism (61 versus 76). Because of its smaller size, the Demerjian mechanism runs faster when used in a dispersion model. This slight difference in speed can potentially be significant if a large number of analyses are to be performed.

Second, the acceptance and present use of the mechanism needs to be considered. The CBM-III is presently widely used. It is currently contained in a revised version of the SAI trajectory model and in the EKMA/OZIPM-2 models. EPA has prepared a set of recommendations for use of the CBM-III in performing city specific EKMA analyses (Gipson, 1984). Therefore, the CBM-III mechanism presently is more readily usable for performing photochemical simulations than is the Demerjian mechanism.

Additional model simulations must be performed to validate the mechanisms for methanol photochemistry. The most important simulations will involve modeling smog chamber studies using methanol combustion products as input species. Very few of these types of smog chamber runs presently exist.

No recommendation as to the future use of the CIT mechanism can be made until the cause of the unusual results of the 50% methanol conversion scenario are analyzed and poential problems with the implementation of the mechanism solved. The developers of the CIT mechanism were not able to supply a set of test cases to use to check out the mechanism. A test case is essential if a user is to ensure proper functioning of the mechanism. Such a test case must be obtained prior to further analysis of the CIT mechanism.

6.4 Recommended Additional Analyses

A significant limitation of the mechanism sensitivity analyses was the lack of a test case with which to test proper implementation of the CIT mechanism. Without such a test case, and because of the unusual results obtained for the 50% methanol conversion scenario, there are serious doubts about the proper implementation of the CIT mechanism used in this study. Additional analyses should be performed using the CIT mechanism to determine the cause of the poor performance of the mechanism on the 50% methanol conversion scenarios.

The following additional analyses should be performed for the CIT mechanism.

- Obtain and test a benchmark run to ensure proper functioning of the mechanism.
- Obtain a test case from the CIT mechanism developers closely duplicating the 50% methanol conversion scenario.
- Based upon the results of the first two test cases, execute additional test cases to pinpoint the source of any potential problems.

Model sensitivity analyses should be expanded beyond those few cases performed for this study. These sensitivity runs should include the following cases.

- Both mechanisms should be run over a two-day period to look at the dynamics of ozone formation on the second day. As discussed in Section 2.3.4, methyl nitrite (and formaldehyde) will tend to accumulate overnight. Both will tend to photodissociate after sun rise leading to a potentially large radical population during the morning of the second day. The initial second day conditions modeled should be identical to those of the first day and the subsequent differences monitored as a function of time. Species of interest to monitor hour by hour include: ozone, PAN, NO, NO_2, HO, HO_2, and the total radical population.

- Several runs should be made assuming different levels of hydrocarbon concentrations, both initial and those due to emissions. These runs would be used to check the results of Jeffries, et al (1981) that ozone reduction is approximately linearly proportional to hydrocarbon reduction.
- Additional runs should be made examining the sensitivity of each mechanism to background and aloft hydrocarbon and ozone concentrations.
- Different mechanisms make different assumptions concerning computation of photolytic rate constants. The sensitivity of methanol chemistry to various photolytic rate constants should be investigated. Of particular concern are the rate constants used for formaldehyde and higher aldehydes since these species play a major role in photochemistry and their concentrations in the atmosphere may be significantly altered by methanol conversion.

6.5 References for Section 6.0

Dodge, M. (1984): Letter from Marcia Dodge (RTP, EPA) to Phillip Lorang (EPA, Ann Arbor) expressing EPA's concurrence with the additions to the photochemical reaction sets to account for methanol, May 9, 1984.

Gipson, G.L., (1984): Guideline for Using the Carbon Bond Mechanism in City-Specific EKMA, EPA Report EPA-450/4-84-005, U.S. EPA, Research Triangle Park, NC, February 1984.

Jeffries, H.E., K.G. Sexton, and C.N. Salmi (1981): The Effects of Chemistry and Meteorology on Ozone Control Calculations Using Simple Trajectory Models and the EKMA Procedure. Report to U.S. EPA by the University of North Carolina under Contract No. 68-02-3523. EPA report No. EPA-450/4-81-034.

APPENDIX A

CHEMICAL MECHANISMS USED
IN SENSITIVITY ANALYSIS

APPENDIX A

This appendix contains a brief discussion of GCKM's treatment of chemical mechanisms, followed by a listing of each mechanism as it was input to the model.

To define the mechanism to be simulated, the GCKM expects to receive a group of cards, one card for each reaction, terminated by a blank card. Each card is of the form

$$r_1R_1 + r_2R_2 + r_3R_3 = p_1P_1 + p_2P_2 + p_3P_3 + p_4P_4 + p_5P_5 \quad k_1, k_2F$$

where r = coefficient for the reactant R
p = coefficient for the product P
k_1, k_2 = reaction rates
F = indicates the parameters upon which the reaction rates depend

The reaction itself has the following restrictions on its format:

- R and P are species names (alphanumeric, first character alphabetic, only first four characters recognized).
- r and p can be written in I or F format (each coefficient must be less than 20 characters in length).
- Embedded blanks are ignored.
- Missing coefficients are assumed to be equal to one.
- Each species and coefficient pair must be separated by a "+" sign (except reactants and products separated by "=").
- The reaction must be separated from the reaction rate portion of the input by at least one space.
- The reaction set must be terminated by a blank card.
- There can be three or less reactants and five or less products.

Note that it is possible to have only one reactant and no product or only one product and no reactant. This allows the existence of permanent sinks or sources independent of other species. This is an important capability when modeling smog chamber data where extra reactions of this form can be used to simulate wall effects.

The reaction rate parameters k_1, k_2, and F specify the reaction rate and the parameters that the reaction rate can depend on. The following dependencies are allowed:

- ultraviolet (UV) radiation
- total solar radiation (TSR)
- temperature
- water vapor concentration

If there are no dependencies (i.e., constant reaction rate) the only parameter required is k_2. If the reaction rate depends on UV, TSR, or temperature, then the rate parameters are given as

- k_1, k_2U (for UV)
- k_1, k_2S (for TSR)
- k_1, k_2T (for temperature)

Unless water vapor is explicitly present in the reaction, water vapor dependence can be indicated by putting a "W" at the end:

- k_1, k_2UW
- k_1, k_2SW
- k_1, k_2TW

The water dependence is included so that the explicit handling of water vapor in the reactions can be ignored. If water is explicitly present in the reactions, the "W" option should not be used.

The following formulas are used by the model to give the actual reaction rate (k):

$$k = k_1 \text{ (UV or TSR)}^{k_2}$$

$$k = k_1 \exp (k_2/T)$$

The use of the "W" option instructs the program to multiply the reaction rate by the water vapor concentration.

The following format requirements are assumed by interpreting programs for the reaction rate parameters:

- The parameter group is separated from the reaction itself by at least one space.
- k_1 and k_2 are separated by a comma (if k_2 required).
- No embedded spaces are allowed in the parameter groups.
- k_1 and k_2 can be expressed in an integer, floating point or exponential format (each parameter $\leq$ 20 characters).
- If the "W" option is used, it must be the last character.

If a card's reaction or rate cannot be interpreted, the card image is printed and execution is stopped.

LISTING OF CBM-III MECHANISM
AS INPUT TO GCKM

CBM-III

```
 1:NO2=NO+O 1.,1.U
 2:O=O3 4.4E6
 3:NO+O3=NO2 3452,-1450T
 4:NO2+O3=NO3 178.6,-2450T
 5:NO2+O=NO 1300U
 6:OH+O3=HO2 2867,-1000T
 7:HO2+O3=OH 400.6,-1525T
 8:OH+NO2=HNO3 16000
 9:OH+CO=HO2 440
10:2NO=2NO2 1.5E-4
11:NO+NO3=2NO2 28000
12:NO2+NO3=2HNO3 4.63E-19,1.06E4TW
13:NO+HO2=NO2+OH 12000
14:2HO2=H2O2 15000
15:X+PAR= 1.E5
16:OH+PAR=MEO2 7858,-560T
17:O+OLE=MEO2+ACO3+X 8035,-325T
18:O+OLE=CARB+PAR 8035,-325T
19:OH+OLE=RAO2 6043,540T
20:O3+OLE=CARB+CRIG 4.67,-1900T
21:O3+OLE=CARB+MCRG+X 4.67,-1900T
22:O+ETH=MEO2+HO2+CO 8791,-800T
23:O+ETH=CARB+PAR 8791,-800T
24:OH+ETH=RBO2 3330,382T
25:O3+ETH=CARB+CRIG 12.91,-2560T
26:NO+ACO3=NO2+MEO2 1.04E4
27:NO+RBO2=NO2+2CARB+HO2 12000
28:NO+RAO2=NO2+2CARB+HO2 1.2E4
29:NO+MEO2=NO2+CARB+MEO2+X 3700
30:NO+MEO2=NO2+CARB+HO2 7400
31:NO+MEO2=NRAT 900
32:O3+RBO2=2CARB+HO2 5
33:O3+RAO2=2CARB+HO2 20
34:OH+CARB=CRO2+X 100
35:OH+CARB=HO2+CO 9000
36:OH+CARB=ACO3+X 8200
37:CARB=CO+H2 .00333,1.377U
38:CARB=1.333333HO2+CO+.6666667MEO2+.6666667X .00359,1.661U
39:NO2+ACO3=PAN 7000
40:PAN=ACO3+NO2 1.04E18,-13500T
41:HO2+ACO3= 1.5E4
42:HO2+MEO2= 9000
43:NO+CRIG=NO2+CARB 1.2E4
44:NO2+CRIG=NO3+CARB 8000
45:CARB+CRIG= 2000
46:NO+MCRG=NO2+CARB+PAR 1.2E4
47:NO2+MCRG=NO3+CARB+PAR 8000
48:CARB+MCRG= 2000
49:CRIG=CO 670
50:CRIG= 240
51:CRIG=2HO2+CO 90
52:MCRG= 150
53:MCRG=MEO2+OH+CO 340
54:MCRG=MEO2+HO2 425
55:MCRG=CARB+2HO2+CO 85
56:OH+ARO=RARO 4.493E4,-600T
57:OH+ARO=HO2+OPEN 5.55E4,-400T
58:NO+RARO=NO2+PHEN+HO2 4000
59:OPEN+NO=NO2+DCRB+X+APRC 6000
60:APRC=DCRB+CARB+CO+X 1.E4
61:APPC=2CARB+2CO 1E4
62:PHEN+NO3=PHO+HNO3 5000
63:PHO+NO2=NPHN 4000
64:PHO+HO2=PHEN 5E4
65:OPEN+O3=DCRB+X+APRC 40
66:OH+PHEN=HO2+APRC+PAR+CARB 3E4
67:DCRB=HO2+1.0ACO3+1.0CO .0198,.986U
68:PHEN+OH=PHO 1E4
69:CRO2+NO=NO2+CARB+ACO3+X 1.2E4
70:DCRB+OH=ACO3+CO 2.5E4
71:HONO=OH+NO .2059,1.076U
72:OH+NO=HONO 9770
73:O3=O1D .0172,3.098U
74:O1D=O 4.44E10
75:O1D=2OH 3.4E5W
76:OH=HO2 58
77:OH=MEO2 28
78:NR=NR 1
79:O3=O .0533,.734U
80:CH4O+OH=HO2+HCHO 1500.
81:HCHO+OH=HO2+CO 15000.
82:HCHO=HO2+HO2+CO 2.71E-3,1.U
83:HCHO=H2+CO 3.76E-3,1.U
84:MONO=CH3O+NO 0.3,1.U
85:CH3O+NO=MONO 4.40E4
86:CH3O=HCHO+HO2 1.88
```

LISTING OF CIT MECHANISM
AS INPUT TO GCKM

CIT

```
 1:NO2=NO+O 1.,1.U
 2:O=O3 7.896E5,5.1E2T
 3:NO+O3=NO2 3.10E3,-1450T
 4:O+NO2=NO 1.34E4
 5:O+NO=NO2 5.600E2,5.840E2T
 6:O+NO2=NO3 3.590E3
 7:O3+NO2=NO3 1.740E2,-2.450E3T
 8:NO+NO3=2NO2 2.700E4
 9:NO2+NO3=N2O5 7382.
10:N2O5=NO2+NO3 3.44E16,-1.06E4T
11:N2O5=2HNO3 1.50E-5W
12:NO+OH=HNO2 1.70E4
13:HNO2=OH+NO 1.84E-1,1.U
14:NO2+HO2=HNO2 5.81E-2,1.006E3T
15:HNO2+OH=NO2 9.77E3
16:NO2+HO2=HNO4 5.81E1,1.006E3T
17:HNO4=HO2+NO2 1.80E15,-9950T
18:NO+HO2=NO2+OH+CON1 1.200E4
19:RO2+NO=NO2+RO+CON2 1.200E4
20:RCO3+NO=HO2+RO2+CON3 3.79E3
21:NO2+OH=HNO3 1.52E4
22:OH+CO=HO2 4.40E2
23:O3=O 7.13E-2,1.U
24:O3+OH=HO2 2.22E3,-1.00E3T
25:O3+HO2=OH 16.27,-580T
26:2HO2=H2O2 8.28E3
27:H2O2=2OH 2.56E-3,1.U
28:HCHO=2HO2+CO+NEW1 3.75E-3,1.U
29:HCHO=CO 8.10E-3,1.U
30:OH+HCHO=HO2+CO 1.389E4
31:RCHO=RO2+HO2+CO 3.20E-3,1.U
32:OH+RCHO=RCO3 2.570E4
33:ETH+OH=RO2 1.160E4
34:ETH+O=RO2+HO2 1.220E3
35:OLE+OH=RO2 5.950E4
36:OLE+O=RO2+RCO3 9.93E3
37:OLE+O3=0.27OH+RCHO+0.61HO2 .056
38:OLE+O3=0.37RO+HCHO+0.61RO2 .056
39:ALK+OH=RO2 6.06E3
40:ALK+O=RO2+OH 99.8
41:OH+ARO=RO2+RCHO 2.21E4
42:RO=0.5RCHO+0.5HCHO+HO2 2.00E5
43:RO+NO=RONO 1.47E4
44:RONO=RO+NO 0.22,1.U
45:RO+NO2=RNO3 7.35E3
46:RO+NO2=RCHO+HNO2 639.
47:RO2+NO2=RNO4 5.50E3
48:RNO4=NO2+RO2 1.80E15,-9950T
49:RO2+NO2=RCHO+HNO3 5.50
50:RO2+RO2=2RO 68.5,223.T
51:RCO3+NO2=PAN 2.07E3
52:PAN=NO2+RCO3 4.77E16,-1.252E4T
53:NR=NR 1.00E6
54:CH4O+OH=HO2+HCHO 1500.
55:MONO=CH3O+NO 0.3,1.U
56:CH3O+NO=MONO 4.40E4
57:CH3O=HCHO+HO2 1.88
```

LISTING OF DEMERJIAN MECHANISM
AS INPUT TO GCKM

DEMERJIAN

```
 1:NO2=NO+O 1.,1.U
 2:O=O3 4.73E6
 3:O3+NO=NO2+O2 3250.,-1430.T
 4:O3+NO2=NO3+O2 177.,-2450T
 5:O3=O1D+O2 0.013,2.44U
 6:O1D=O 4.23E10
 7:O1D=2HO 3.4E5W
 8:NO3+NO=2NO2 2.96E4
 9:NO3+NO2=N2O5 1780.
10:N2O5=NO3+NO2 3.11
11:N2O5=2HNO3 1.92E-5W
12:HONO=HO+NO .205,1.043U
13:HO+CO=HO2+CO2 414.
14:HO2+NO2=HONO+O2 4.40
15:HO2+NO=HO+NO2 5470.,240.T
16:HO2+NO2=HO4N 1.52E3
17:HO4N=HO2+NO2 3.26
18:HO+HONO=NO2+H2O 9750.
19:HO+NO2=HNO3 1.49E4
20:HO+NO=HONO 7.35E3
21:HO+HNO3=NO3 22.2,650T
22:HO2+O3=HO+2O2 20.7,-580.T
23:HO+O3=HO2+O2 2360.,-940.T
24:HO2+HO2=H2O2+O2 66.5,1200.T
25:H2O2=2HO .00143,1.598U
26:ETH+O3=.4RO2+HCHO+.1HO2 2.5E-3
27:ETH+HO=FRO2+HCHO 12000.
28:OLE+O=RO2+ALD+HO2 5100.
29:OLE+O3=.75RO2+.75ALD+.4HO2 9.5E-2
30:OLE+HO=RO2+.75ALD+.25HCHO 55000.
31:PAR+HO=RO2 5000.
32:HCHO=CO .006,1.26U
33:HCHO=2HO2+CO .0051,1.54U
34:HCHO+HO=HO2+H2O+CO 16000.
35:RO2+NO=RO+NO2 11000.
36:RO=.75ALD+HO2+.25HCHO 1.55E8,-2000.T
37:ALD=RO2+HO2+CO .0014,1.76U
38:ALD+HO=R1O2+H2O 24000.
39:FRO2+NO=FRO+NO2 11000.
40:FRO=HCHO+HO2 2.27E5
41:R1O2+NO2=PAN 8870.
42:PAN=R1O2+NO2 3.6E18,-13330.T
43:RO+NO2=RNO3 100.
44:RO2+O3=RO+2O2 2.00
45:R1O2+NO=RO2+NO2 20700.
46:TOL+HO=RTO2+ALD+DCB1 8700.
47:ARO+HO=RXO2+ALD+DCB1 34000.
48:RTO2+NO=RTO+NO2 11000.
49:RTO=DCB1+HO2+CO 1.86E5
50:RXO2+NO=RXO+NO2 11000.
51:RXO=DCB2+HO2+CO 1.86E5
52:DCB1=2CO+2HO2 .004,1.U
53:DCB1=.20HCHO+1.80CO .004,1.U
54:DCB1+HO=HO2+2CO 17000.
55:DCB2=R1O2+HO2+2CO .0088,.918U
56:DCB2=.50ALD+.50HCHO+.50FRO2 .0088,.918U
57:DCB2+HO=R1O2+CO 25600.
58:RTO2+O3=RTO+2O2 2.00
59:RXO2+O3=RXO+2O2 2.00
60:R1O2+O3=RO2+2O2 2.00
61:OLE+O3=COOH+ALD 1.50E-3
62:CH4O+HO=HO2+HCHO 1500.
63:MONO=CH3O+NO 0.3,1.U
64:CH3O+NO=MONO 4.40E4
65:CH3O=HCHO+HO2 1.88
```

APPENDIX B

DESCRIPTION OF SPECIES AND EMISSION FRACTION CALCULATIONS AND SAMPLE CALCULATIONS

B.1 Conversion of Carbon Fractions from CBM-III to CIT and Demerjian Fractions and Species Concentrations

The CBM-III carbon fractions for the initial parcel NMOC concentration and the aloft NMOC concentration were taken from the SAI study (SAI, 1983). These fractions are shown in Table B-1. The CBM-III fractions were converted to carbon fractions for the CIT and Demerjian mechanisms using the procedure shown in Table B-1. The procedure is not exact since the original species profile used by SAI to calculate CBM-III fractions was not available.

The calculation procedure makes use of "typical" urban carbon fractions for the CIT and CBM-III mechanisms (McRae *et al*, 1983). These fractions, shown in Table B-1, were derived from the same initial species profile. The underlying assumption in our procedure is that the ratio of corresponding species fractions for two mechanisms (OLE/OLE, ALK/PAR, etc.) will be approximately the same for all urban VOC samples.

Since the procedure is an approximation, the total carbon fraction obtained by summing the fractions for each species does not equal 1.0. To correct this, each computed species fraction was normalized by dividing by the summed total carbon fraction.

This procedure does not necessarily yield the same CIT and Demerjian carbon fractions that would have been calculated had the original species profiles used by SAI been available. However, a single urban species profile could be developed that would yield the given CBM-III and computed CIT carbon fractions in Table B-1. Therefore, the procedure is reasonable for the purposes of this study.

Species concentrations were calculated from the carbon fractions in Table B-1 and the assumed initial NMOC concentration (0.5 ppmC). This procedure is shown in Table B-2 for the CIT and Demerjian mechanisms. The only difference between the lumping procedures for these mechanisms is that Demerjian splits the ARO fraction into 60% ARO and, 40% TOL (toluene). The

TABLE B-1. CALCULATION OF CIT CARBON FRACTIONS FROM CBM-III CARBON FRACTIONS

Species	CBM-III Carbon Fraction for Los Angeles[a]		Typical Urban CIT Carbon Fraction		Typical Urban CBM-III Carbon Fraction[b]		Preliminary CIT Carbon Fraction for Los Angeles		Normalizing Factor		Normalized CIT Carbon Fraction for Los Angeles
OLE	0.051	x	0.051	÷	0.011	=	0.24	÷	1.21	=	0.20
ALK (PAR)	0.725	x	0.30	÷	0.32	=	0.68	÷	1.21	=	0.56
ARO	0.126	x	0.11	÷	0.072	=	0.19	÷	1.21	=	0.16
ETH	0.062	x	0.021	÷	0.021	=	0.062	÷	1.21	=	0.051
HCHO (CARB)	0.036	x	0.0093	÷	0.025	=	0.013	÷	1.21	=	0.011
RCHO (CARB)	0.036	x	0.014	÷	0.025	=	0.020	÷	1.21	=	0.017
TOTAL	1.00		0.51[c]		0.45[c]		1.21				1.00

[a] SAI (1983). Also presented in Table B-3.

[b] Computed from data in Table 42 of McRae *et al*, 1983.

[c] A non-reactive fraction of ~0.50 is not included; therefore, the total is less than 1.0.

TABLE B-2. CALCULATION OF CIT AND DEMERJIAN NMOC SPECIES CONCENTRATIONS

Species	Carbon Fraction[a]		Total NMOC Conc. (ppmC)		Carbon Number[b]		Species Conc. (ppmV)
OLE	0.20	x	0.50	÷	5.24	=	0.019
ALK	0.56	x	0.50	÷	4.56	=	0.062
ARO	0.16	x	0.50	÷	7.56	=	0.0104[c]
ETH	0.051	x	0.50	÷	2.00	=	0.0133
HCHO	0.011	x	0.50	÷	1.00	=	0.0055
RCHO	0.017	x	0.50	÷	2.24	=	0.0038

[a] Computed in last column of Table B-1.

[b] CIT Carbon Numbers from McRae _et al_ (1983).

[c] For Demerjian mechanism, ARO species conc. split 60% ARO, 40% TOL (toluene).

TABLE B-3. CBM-III CARBON FRACTIONS USED FOR LOS ANGELES AREA[a]

	City Center			
Species	Gasoline Powered Vehicles	Stationary Sources	Combined[b]	Aloft
OLE	0.0753	0.0300	0.051	0.004
PAR	0.6750	0.7678	0.725	0.694
ARO	0.1475	0.1083	0.126	0.051
ETH	0.0291	0.0409	0.062	0.032
CARB	0.0731	0.0530	0.036	0.219

[a] SAI (1983).

[b] Combined Carbon Fractions are weighted average of gasoline powered vehicle and stationary source emission carbon fractions.

same procedure was performed for the CBM-III mechanism using the corresponding CBM-III carbon fractions given by SAI.

The procedure presented in Tables B-1 and B-2 is for the base case inputs to the CIT mechanism shown in Table 5-5 of the main body of the report. For each test case, the NMOC emissions were assumed to occur from three sources: 1) stationary sources; 2) gasoline powered vehicles; and 3) methanol powered vehicles. The same calculation procedure was followed for the first two components, using the respective CBM-III carbon fractions taken from the SAI study (SAI, 1983) and shown in Table B-3. The NMOC due to methanol combustion was split among HCHO, CH_3OH, and $MeNO_3$ as described in the report.

Using the procedures described above, the initial concentrations for each species were determined separately for the stationary sources, gasoline powered vehicles, and methanol powered vehicles, for a given sensitivity case. The initial concentrations for each species were then added together to produce the total initial concentration for each species for the given sensitivity test case.

B.2 Emissions Fraction Calculation

1. Calculate moles of species for each hour and divide by area of air parcel for each mechanism to calculate initial emission density (Q_i).

$$Q_i = \frac{\text{Moles (NMOC)/day}}{\text{Parcel Area x 24 hours/day}}$$

NMOC = 196000 moles/day
Parcel Area = 25 km^2

$$Q_i = \frac{\text{328 moles NMOC}}{km^2}$$

2. Now calculate Q_o where Q_c is the initial emissions density needed to produce the initial air parcel concentration in one hour.

$$Q_o = \alpha \, C_o H_o$$

and

H_o = initial mixing height = (70.1m)

C_o = initial air parcel concentration = 0.5 ppmV NMOC

$$\alpha = \frac{\text{1 mole NMOC}}{10^6 \text{ mole air - ppmV}} \times \frac{\text{1 mole air}}{\text{24.4 L}} \times \frac{10^{12}\text{ L}}{\text{km}^3}$$

$$= \frac{\text{41,000 moles NMOC}}{\text{km}^3 \text{ - ppmV}}$$

$$Q_o = \frac{\text{41,000 moles NMOC}}{\text{km}^3\text{-hr-PPMV}} \times (0.5 \text{ ppm}) \times (0.0701 \text{ km})$$

$$= \frac{\text{1,437 moles NMOC}}{\text{km}^2\text{-hr}}$$

3. Now calculate hourly emission fraction (E_i).

$$E_i = \frac{Q_i}{Q_o}$$

$$E_i = \frac{328 \ \frac{\text{moles}}{\text{km}^2\text{-hr}}}{1437 \ \frac{\text{moles}}{\text{km}^2\text{-hr}}} = 0.23$$

4. The above computed emissions fraction of 0.23 was assumed to be constant for each mechanism for each scenario modeled. Implicit in this assumption are the following assumptions.

   a) The initial parcel concentrations are due to previous emissions.

   b) The carbon (or species) fractions are the same for the emissions and the initial concentrations for each species.

   c) By adjusting the parcel initial concentrations for each species according to the emissions scenario, the subsequent emissions are a constant fraction of these initial concentrations (for each species).

   d) The total mass of NMOC emissions does not change with scenario modeled.

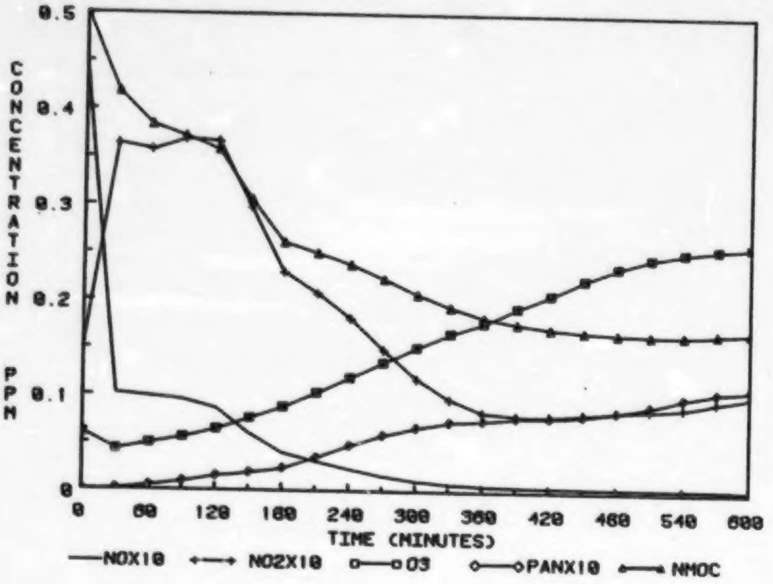
APPENDIX C

PLOTS OF VARIOUS SPECIES FOR EACH MODEL SENSITIVITY RUN

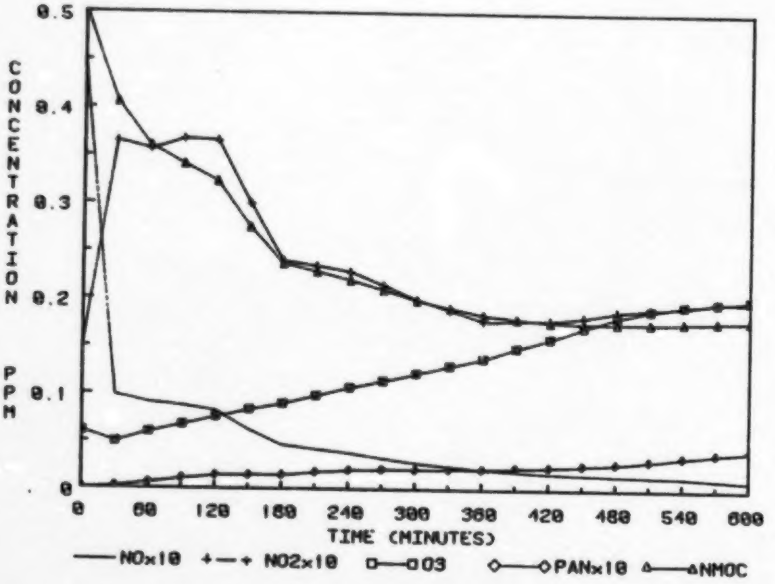
TABLE C-1. IDENTIFICATION PLOTS FOR MODEL SENSITIVITY RUNS

Run Number	Plot Title
1	CB III Chemistry Base Case
2	CIT Chemistry Base Case
3	Demerjian Chemistry Base Case
4	CB III Chemistry 50% Case
5	CIT Chemistry 50% Case
6	Demerjian Chemistry 50% Case
7	CB III Chemistry 100% Case
8	CIT Chemistry 100% Case
9	Demerjian Chemistry 100% Case
10	CB III Chemistry Surface 03=.06 Aloft 03=.04 All Methanol Vehicles
10A	CB III Chemistry Surface 03=.03 Aloft 03=.04 All Methanol Vehicles
11	CIT Chemistry Surface 03=.06 Aloft 03=.04
11A	CIT Chemistry Surface 03=.03 Aloft 03=.04
12	Demerjian Chemistry Surface 03=.06 Aloft 03=.04
12A	Ozone Aloft 03=0.04 ppm Surface 03=0.03 Demerjian Chemistry
13	CB III Chemistry HCHO/MENO$_3$ = 10%/5% With All Methanol Vehicles
14	CIT Chemistry HCHO/MENO$_3$ = 10%/5% With All Methanol Vehicles
15	Demerjian Chemistry HCHO/MENO$_3$ = 10%/5% With All Methanol Vehicles
16	CB III Chemistry HCHO/MENO$_3$ = 20%/1% With All Methanol Vehicles
17	CIT Chemistry HCHO/MENO$_3$ = 20%/1% With All Methanol Vehicles
18	Demerjian Chemistry HCHO/MENO$_3$ = 20%/1% With All Methanol Vehicles
19	CB III Chemistry HCHO/MENO$_3$ = 20%/5% With All Methanol Vehicles
20	CIT Chemistry HCHO/MENO$_3$ = 20%/5% With All Methanol Vehicles
21	Demerjian Chemistry HCHO/MENO$_3$ = 20%/5% With All Methanol Vehicles

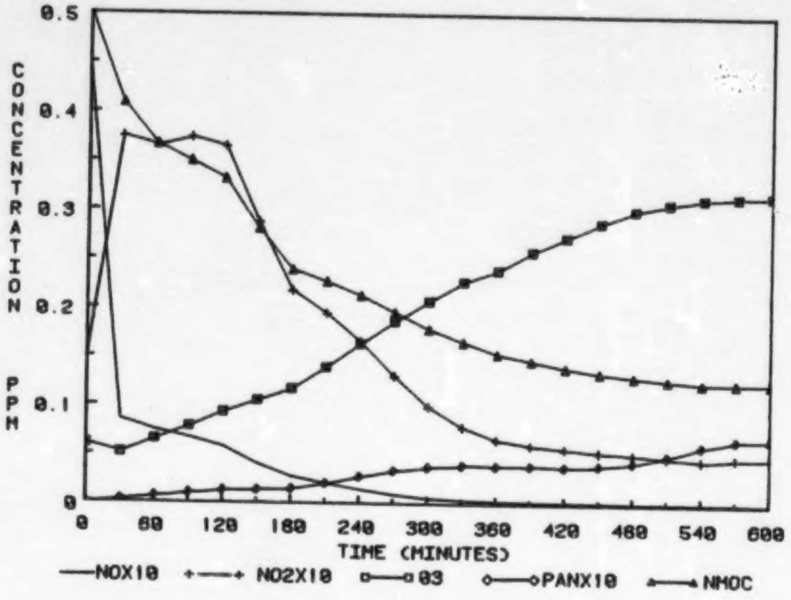
CBIII CHEMISTRY BASE CASE



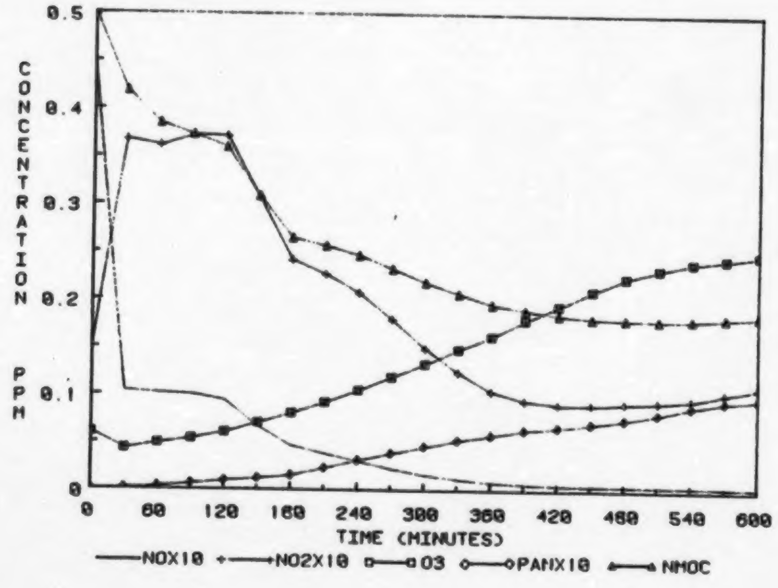
CIT CHEMISTRY BASE CASE



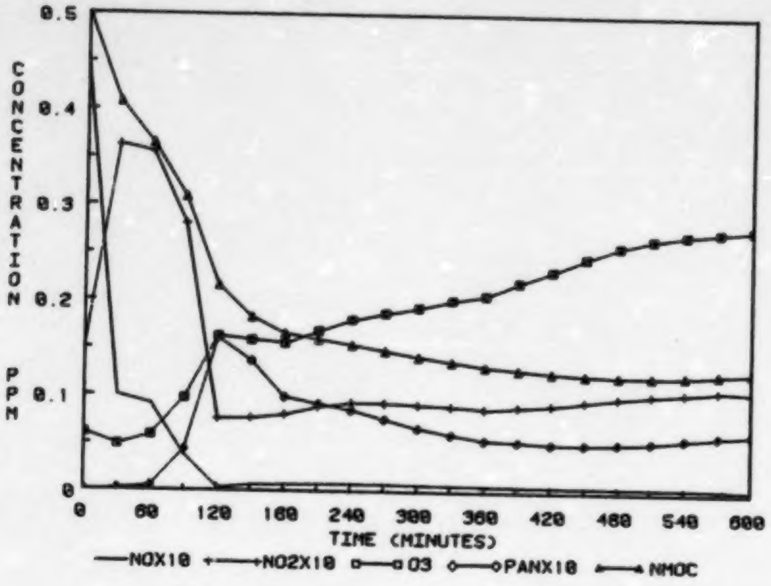
DEMERJIAN CHEMISTRY BASE CASE



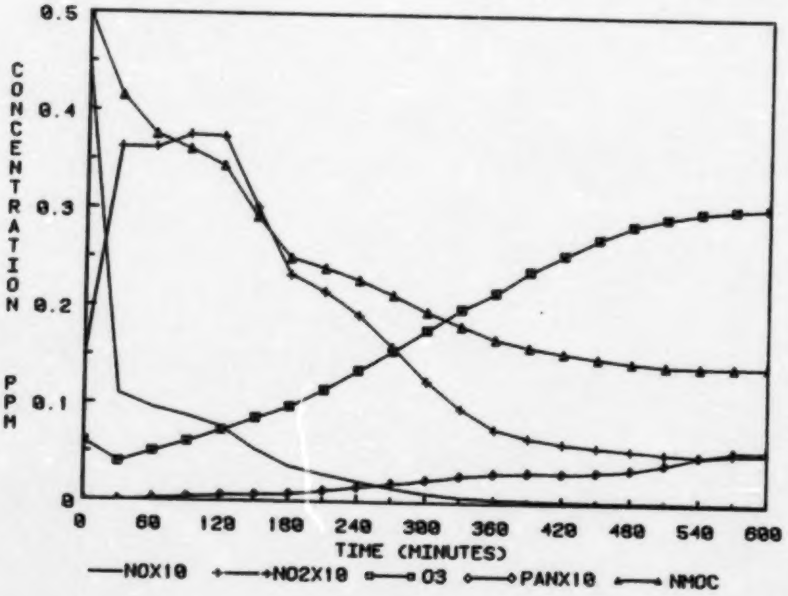
CBIII CHEMISTRY 50% CASE

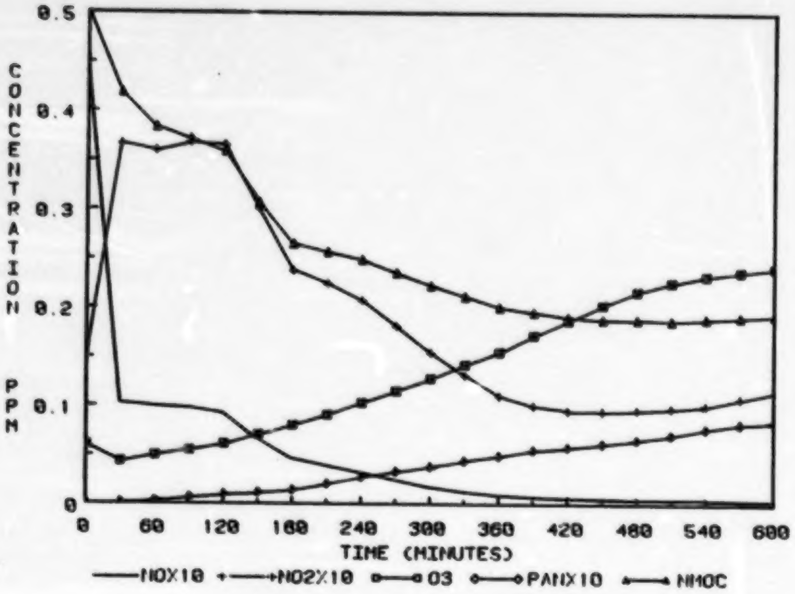


CIT CHEMISTRY 50% CASE

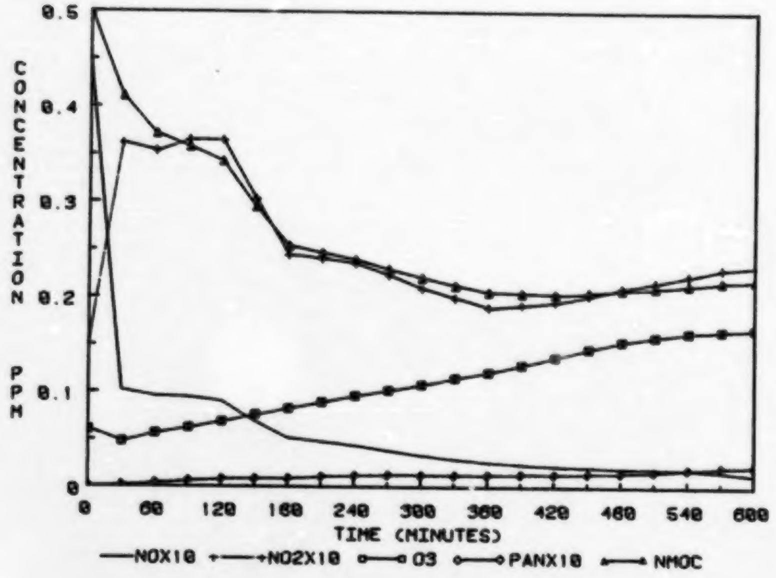


DEMERJIAN CHEMISTRY 50% CASE



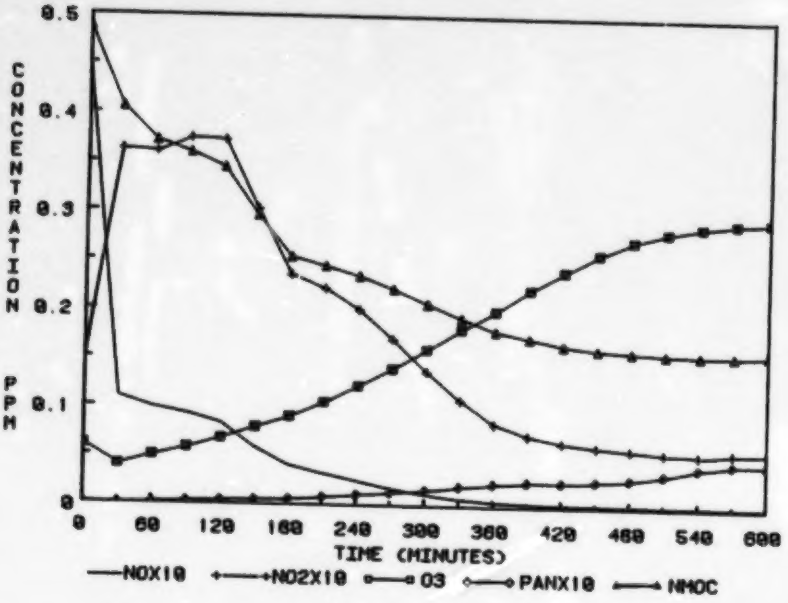


CBIII CHEMISTRY 100% CASE

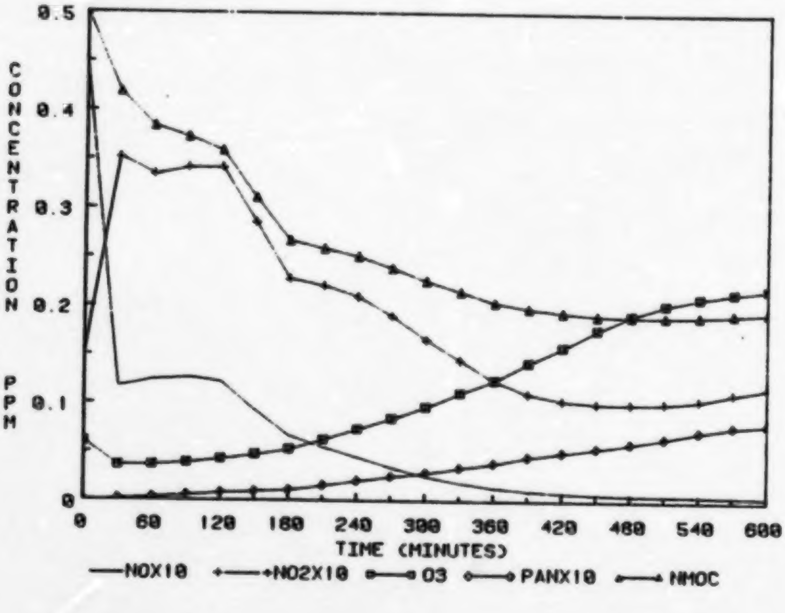


CIT CHEMISTRY 100% CASE

DEMERJIAN CHEMISTRY 100% CASE



CBIII CHEM O3 CASE; SURF O3=.06; ALOFT O3=.04; ALL METHANOL VEHICLES



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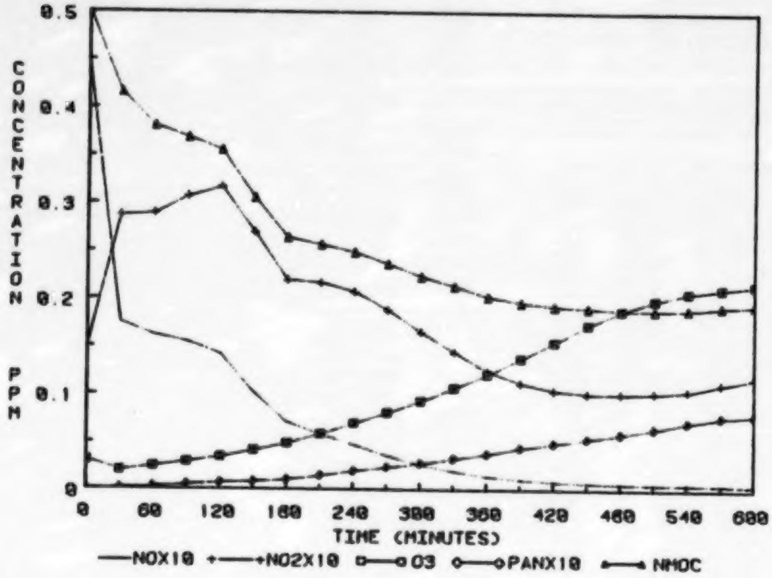
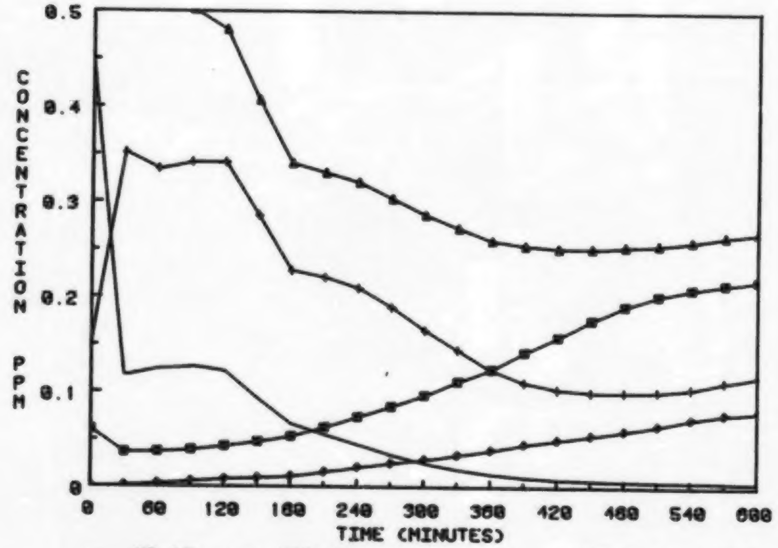
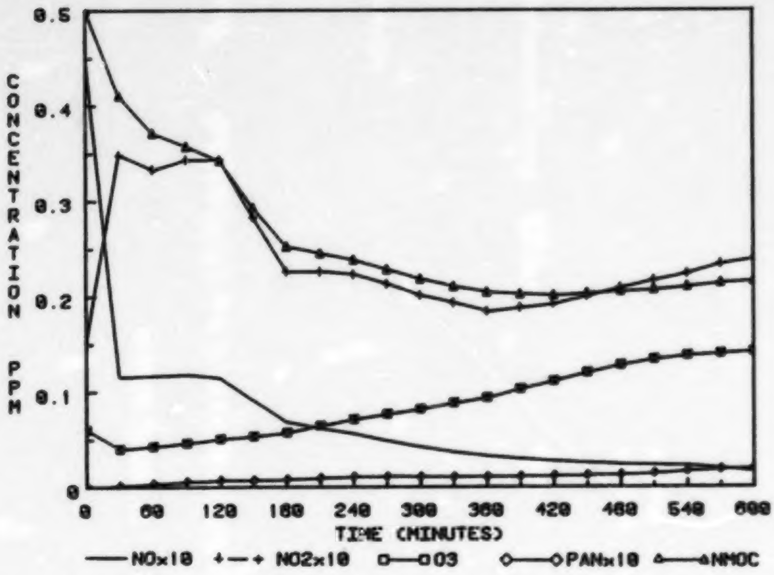


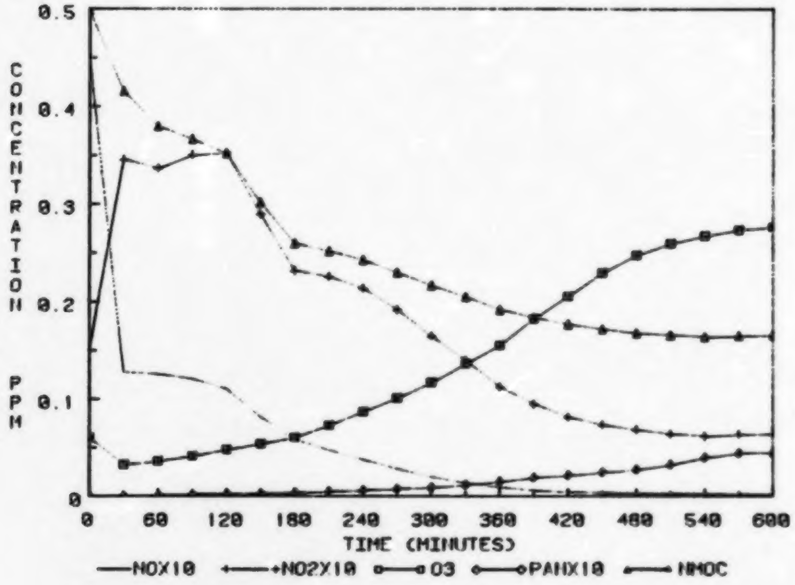
CIT CHEM O3 CASE; SURF O3=.00; ALOFT O3=.04; ALL METHANOL VEHICLES

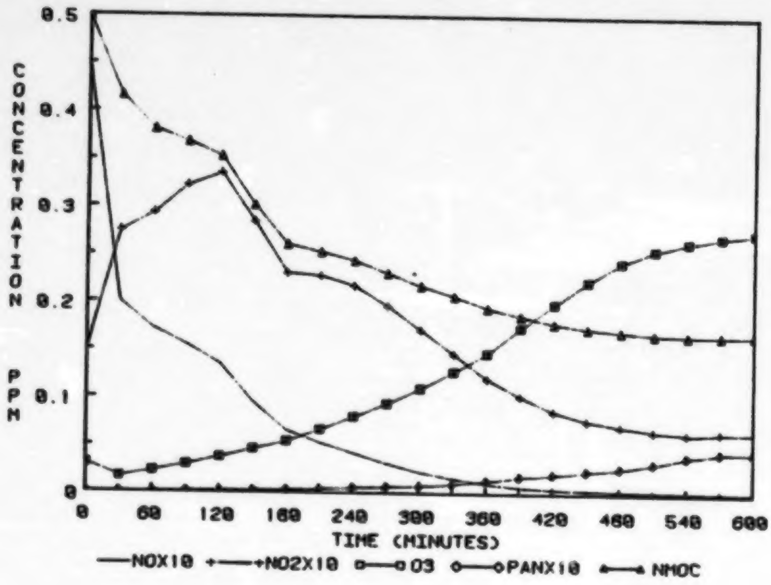


CIT CHEM O3 CASE; SURF O3=.03; ALOFT O3=.04 ALL METHANOL VEHICLES

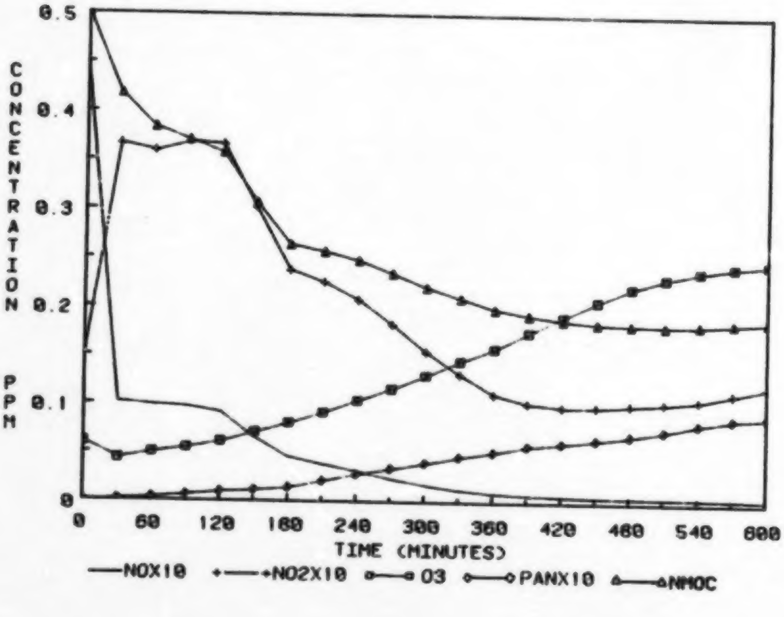


DEMJ CHEM O3 CASE; SURF O3=.08; ALOFT O3=.04; ALL METHANOL VEHICLES



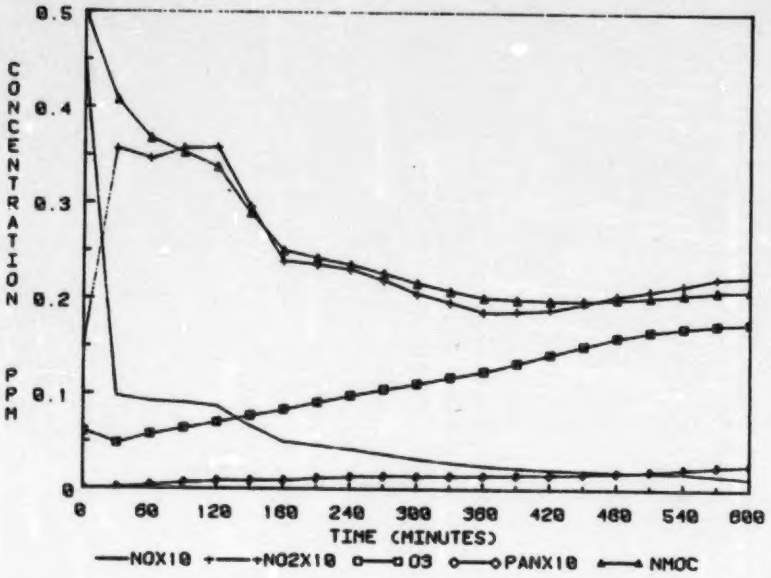


DEMJ CHEM O3 CASE; SURF O3=.03; ALOFT O3=.04; ALL METHANOL VEHICLES

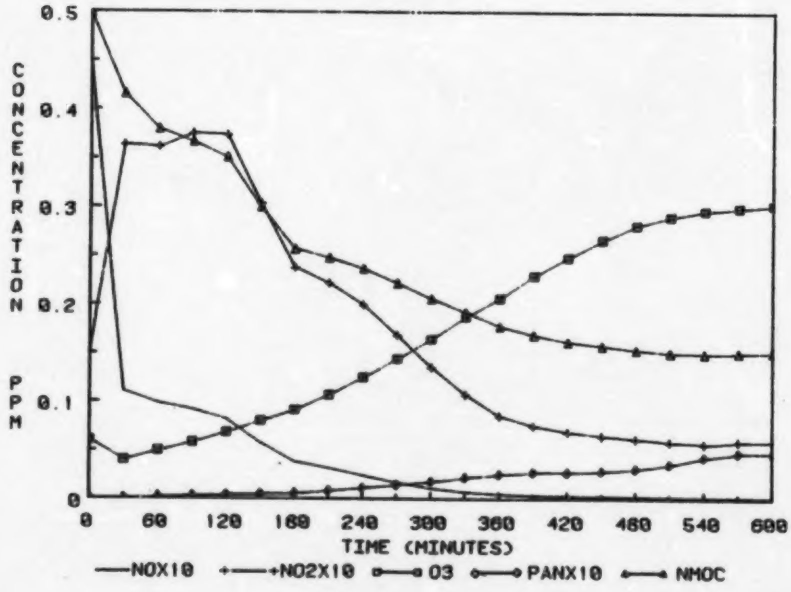


CBIII CHEM HCHO/MENO2=10%/5% ALL METHANOL VEHICLES

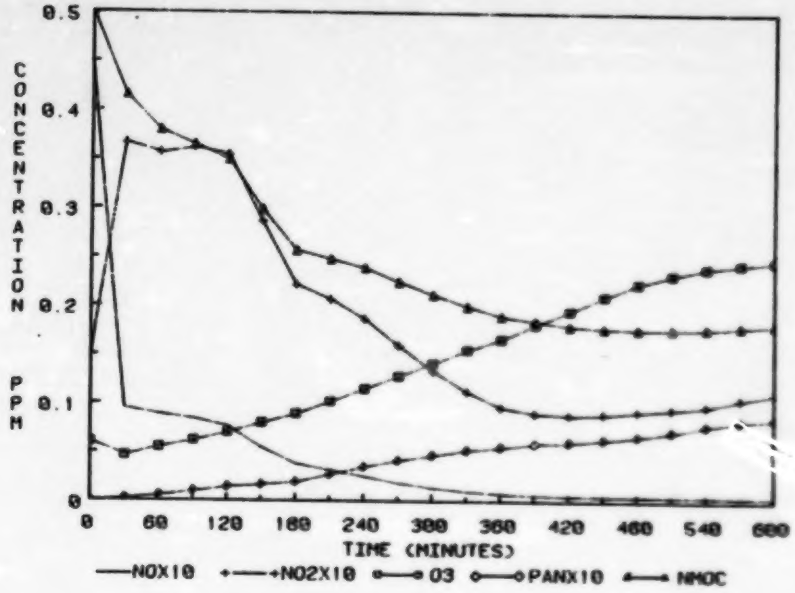
CIT CHEM HCHO/MENO2=10%/5% WITH ALL METHANOL VEHICLES



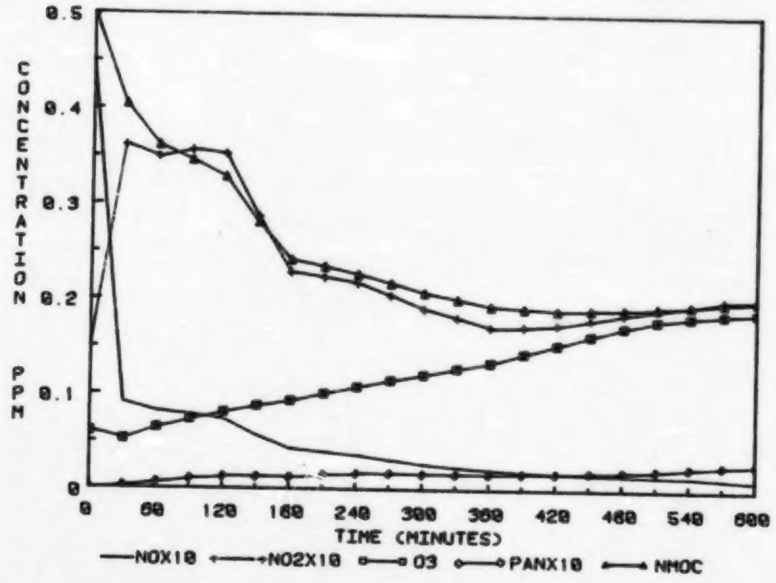
DEMERJIAN CHEM HCHO/MENO2=10%/5% WITH ALL METHANOL VEHICLES



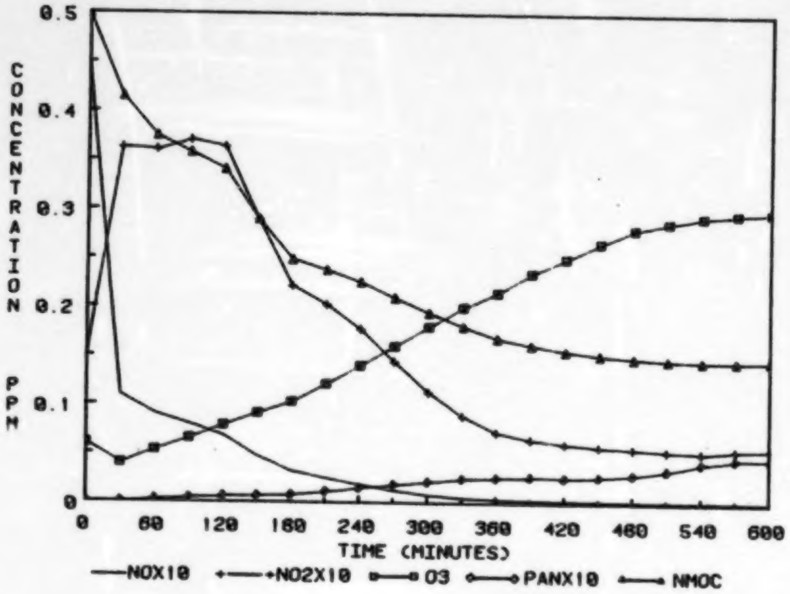
CBIII CHEM HCHO/MENO2=20%/1% WITH ALL METHANOL VEHICLES



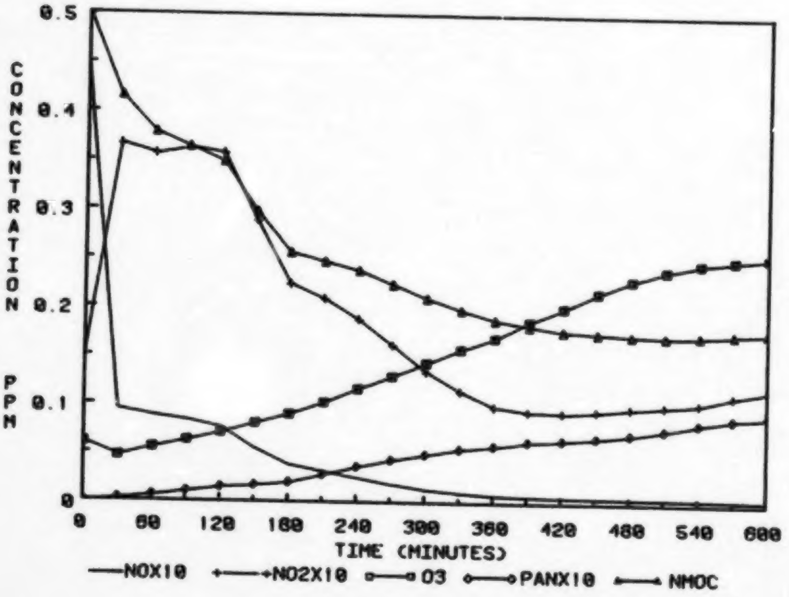
CIT CHEM HCHO/MENO2=20%/1% WITH ALL METHANOL VEHICLES



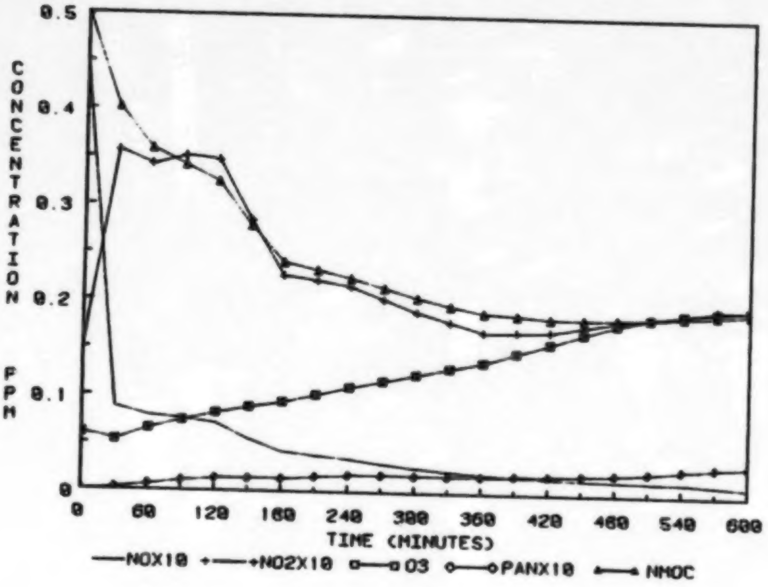
DEMERJIAN CHEM HCHO/MENO2=20%/1% WITH ALL METHANOL VEHICLES



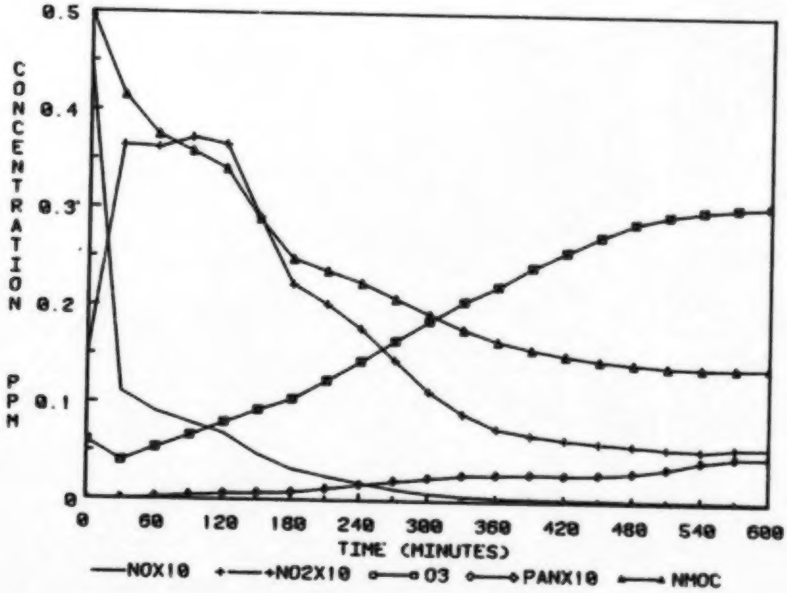
CBIII CHEM HCHO/MENO2=20%/5% WITH ALL METHANOL VEHICLES



CIT CHEM HCHO/MENO2=20%/5% WITH ALL METHANOL VEHICLES



DEMERJIAN CHEM HCHO/MENO2=20%/5% WITH ALL METHANOL VEHICLES



APPENDIX D

CONCENTRATIONS OF VARIOUS SPECIES FOR EACH MODEL SENSITIVITY RUN

```
CBIII CHEMISTRY BASE CASE
            NO        NO2        O3         PAN        NMOC
      0. .450-001 .150-001 .600-001 .000       .501+000
     30. .101-001 .363-001 .428-001 .167-003 .417+000
     60. .980-002 .357-001 .497-001 .504-003 .383+000
     90. .945-002 .368-001 .560-001 .989-003 .371+000
    120. .856-002 .366-001 .645-001 .154-002 .357+000
    150. .592-002 .297-001 .764-001 .191-002 .305+000
    180. .394-002 .229-001 .881-001 .238-002 .260+000
    210. .303-002 .207-001 .103+000 .352-002 .249+000
    240. .227-002 .181-001 .119+000 .477-002 .237+000
    270. .155-002 .148-001 .135+000 .587-002 .222+000
    300. .105-002 .118-001 .151+000 .671-002 .206+000
    330. .752-003 .965-002 .166+000 .731-002 .193+000
    360. .588-003 .831-002 .177+000 .747-002 .182+000
    390. .503-003 .798-002 .193+000 .779-002 .176+000
    420. .460-003 .801-002 .207+000 .783-002 .171+000
    450. .436-003 .826-002 .223+000 .810-002 .168+000
    480. .418-003 .855-002 .236+000 .852-002 .166+000
    510. .410-003 .873-002 .246+000 .914-002 .165+000
    540. .402-003 .896-002 .252+000 .997-002 .165+000
    570. .364-003 .962-002 .256+000 .106-001 .167+000
    600. .309-003 .102-001 .259+000 .109-001 .169+000
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cit chemistry base case
            NO        NO2        O3         PAN        NMOC
      0. .450-001 .150-001 .600-001 .000       .503+000
     30. .974-002 .364-001 .489-001 .243-003 .405+000
     60. .897-002 .356-001 .596-001 .637-003 .359+000
     90. .865-002 .367-001 .675-001 .107-002 .340+000
    120. .812-002 .365-001 .755-001 .141-002 .322+000
    150. .612-002 .299-001 .833-001 .144-002 .274+000
    180. .458-002 .239-001 .898-001 .146-002 .236+000
    210. .415-002 .234-001 .984-001 .178-002 .228+000
    240. .375-002 .228-001 .107+000 .200-002 .219+000
    270. .322-002 .214-001 .114+000 .208-002 .209+000
    300. .275-002 .199-001 .122+000 .208-002 .198+000
    330. .239-002 .188-001 .130+000 .211-002 .190+000
    360. .208-002 .177-001 .138+000 .214-002 .183+000
    390. .187-002 .178-001 .149+000 .230-002 .179+000
    420. .169-002 .178-001 .159+000 .240-002 .176+000
    450. .157-002 .182-001 .171+000 .258-002 .175+000
    480. .147-002 .188-001 .182+000 .280-002 .175+000
    510. .140-002 .191-001 .189+000 .310-002 .175+000
    540. .134-002 .193-001 .194+000 .349-002 .176+000
    570. .113-002 .198-001 .197+000 .386-002 .177+000
    600. .899-003 .196-001 .200+000 .415-002 .178+000
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DEMERJIAN CHEMISTRY BASE CASE
              NO        NO2        O3        PAN       NMOC
     0.  .450-001  .150-001  .600-001  .000      .502+000
    30.  .844-002  .374-001  .511-001  .282-003  .408+000
    60.  .737-002  .365-001  .651-001  .655-003  .366+000
    90.  .663-002  .373-001  .782-001  .100-002  .349+000
   120.  .571-002  .364-001  .931-001  .128-002  .331+000
   150.  .399-002  .287-001  .105+000  .134-002  .280+000
   180.  .268-002  .217-001  .117+000  .146-002  .238+000
   210.  .199-002  .194-001  .139+000  .203-002  .226+000
   240.  .141-002  .165-001  .163+000  .273-002  .212+000
   270.  .882-003  .130-001  .186+000  .334-002  .195+000
   300.  .538-003  .989-002  .207+000  .372-002  .178+000
   330.  .363-003  .783-002  .227+000  .393-002  .165+000
   360.  .273-003  .654-002  .239+000  .387-002  .153+000
   390.  .222-003  .598-002  .258+000  .390-002  .146+000
   420.  .192-003  .564-002  .273+000  .380-002  .139+000
   450.  .171-003  .534-002  .288+000  .399-002  .134+000
   480.  .155-003  .511-002  .301+000  .433-002  .130+000
   510.  .146-003  .480-002  .308+000  .503-002  .127+000
   540.  .138-003  .455-002  .313+000  .603-002  .124+000
   570.  .123-003  .477-002  .315+000  .664-002  .124+000
   600.  .992-004  .482-002  .316+000  .673-002  .124+000
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CBIII CHEMISTRY 50%  CASE
              NO        NO2        O3        PAN       NMOC
     0.  .450-001  .150-001  .600-001  .000      .500+000
    30.  .103-001  .367-001  .428-001  .124-003  .418+000
    60.  .101-001  .361-001  .490-001  .335-003  .384+000
    90.  .995-002  .372-001  .540-001  .642-003  .372+000
   120.  .932-002  .371-001  .606-001  .990-003  .359+000
   150.  .665-002  .306-001  .707-001  .123-002  .308+000
   180.  .459-002  .241-001  .809-001  .156-002  .264+000
   210.  .378-002  .226-001  .924-001  .233-002  .256+000
   240.  .302-002  .207-001  .105+000  .315-002  .246+000
   270.  .223-002  .179-001  .119+000  .389-002  .232+000
   300.  .159-002  .149-001  .133+000  .456-002  .218+000
   330.  .114-002  .124-001  .148+000  .527-002  .206+000
   360.  .836-003  .104-001  .162+000  .580-002  .195+000
   390.  .663-003  .946-002  .179+000  .639-002  .189+000
   420.  .565-003  .905-002  .194+000  .668-002  .184+000
   450.  .514-003  .906-002  .210+000  .707-002  .181+000
   480.  .482-003  .923-002  .224+000  .753-002  .180+000
   510.  .466-003  .937-002  .233+000  .811-002  .179+000
   540.  .456-003  .961-002  .240+000  .887-002  .180+000
   570.  .410-003  .103-001  .244+000  .945-002  .182+000
   600.  .348-003  .109-001  .248+000  .973-002  .184+000
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cit chemistry 50% case
            NO        NO2        O3        PAN       NMOC
    0.  .450-001  .150-001  .600-001  .000      .501+000
   30.  .990-002  .362-001  .482-001  .199-003  .407+000
   60.  .905-002  .355-001  .586-001  .502-003  .364+000
   90.  .372-002  .280-001  .973-001  .427-002  .308+000
  120.  .342-003  .760-002  .162+000  .160-001  .215+000
  150.  .645-003  .766-002  .158+000  .136-001  .182+000
  180.  .738-003  .807-002  .155+000  .983-002  .165+000
  210.  .785-003  .889-002  .168+000  .913-002  .159+000
  240.  .796-003  .930-002  .180+000  .847-002  .153+000
  270.  .754-003  .928-002  .187+000  .757-002  .147+000
  300.  .702-003  .909-002  .193+000  .664-002  .141+000
  330.  .660-003  .895-002  .201+000  .599-002  .136+000
  360.  .618-003  .871-002  .206+000  .543-002  .131+000
  390.  .580-003  .893-002  .220+000  .528-002  .128+000
  420.  .551-003  .917-002  .232+000  .508-002  .125+000
  450.  .534-003  .957-002  .246+000  .508-002  .123+000
  480.  .520-003  .998-002  .258+000  .516-002  .122+000
  510.  .514-003  .103-001  .266+000  .536-002  .122+000
  540.  .503-003  .105-001  .271+000  .570-002  .123+000
  570.  .432-003  .108-001  .274+000  .602-002  .125+000
  600.  .337-003  .106-001  .277+000  .626-002  .127+000
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DEMERJIAN CHEMISTRY 50%  CASE
            NO        NO2        O3        PAN       NMOC
    0.  .450-001  .150-001  .600-001  .000      .499+000
   30.  .109-001  .362-001  .396-001  .300-005  .414+000
   60.  .950-002  .362-001  .509-001  .226-003  .375+000
   90.  .867-002  .375-001  .612-001  .432-003  .360+000
  120.  .758-002  .373-001  .730-001  .596-003  .343+000
  150.  .525-002  .301-001  .857-001  .682-003  .291+000
  180.  .355-002  .232-001  .976-001  .808-003  .249+000
  210.  .277-002  .215-001  .115+000  .115-002  .239+000
  240.  .208-002  .191-001  .135+000  .156-002  .227+000
  270.  .140-002  .159-001  .155+000  .194-002  .212+000
  300.  .881-003  .124-001  .177+000  .231-002  .195+000
  330.  .553-003  .964-002  .199+000  .275-002  .181+000
  360.  .379-003  .757-002  .216+000  .305-002  .168+000
  390.  .282-003  .668-002  .238+000  .315-002  .160+000
  420.  .233-003  .614-002  .255+000  .310-002  .154+000
  450.  .204-003  .577-002  .272+000  .328-002  .149+000
  480.  .183-003  .551-002  .286+000  .357-002  .145+000
  510.  .172-003  .522-002  .294+000  .417-002  .142+000
  540.  .164-003  .501-002  .300+000  .503-002  .141+000
  570.  .145-003  .525-002  .303+000  .553-002  .141+000
  600.  .118-003  .529-002  .305+000  .558-002  .142+000
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CBIII CHEMISTRY 100% CASE
           NO        NO2        O3         PAN        NMOC
   0.  .450-001  .150-001  .600-001  .000       .501+000
  30.  .102-001  .366-001  .433-001  .136-003  .418+000
  60.  .989-002  .359-001  .497-001  .351-003  .383+000
  90.  .972-002  .367-001  .547-001  .645-003  .371+000
 120.  .912-002  .365-001  .610-001  .970-003  .358+000
 150.  .653-002  .300-001  .707-001  .117-002  .306+000
 180.  .455-002  .237-001  .803-001  .144-002  .264+000
 210.  .383-002  .224-001  .908-001  .208-002  .256+000
 240.  .313-002  .207-001  .103+000  .274-002  .248+000
 270.  .237-002  .181-001  .115+000  .331-002  .235+000
 300.  .173-002  .154-001  .128+000  .383-002  .222+000
 330.  .126-002  .131-001  .142+000  .443-002  .211+000
 360.  .937-003  .110-001  .155+000  .492-002  .200+000
 390.  .739-003  .100-001  .172+000  .552-002  .195+000
 420.  .623-003  .952-002  .187+000  .582-002  .190+000
 450.  .562-003  .948-002  .203+000  .618-002  .188+000
 480.  .524-003  .963-002  .217+000  .658-002  .188+000
 510.  .506-003  .979-002  .226+000  .709-002  .187+000
 540.  .496-003  .101-001  .233+000  .775-002  .189+000
 570.  .445-003  .108-001  .237+000  .824-002  .191+000
 600.  .378-003  .115-001  .241+000  .848-002  .193+000
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cit chemistry 100% case
           NO        NO2        O3         PAN        NMOC
   0.  .450-001  .150-001  .600-001  .000       .500+000
  30.  .101-001  .361-001  .474-001  .157-003  .410+000
  60.  .949-002  .353-001  .562-001  .393-003  .371+000
  90.  .936-002  .365-001  .624-001  .644-003  .357+000
 120.  .895-002  .364-001  .688-001  .830-003  .342+000
 150.  .683-002  .303-001  .762-001  .853-003  .294+000
 180.  .512-002  .244-001  .826-001  .893-003  .253+000
 210.  .471-002  .240-001  .895-001  .110-002  .246+000
 240.  .433-002  .235-001  .963-001  .124-002  .239+000
 270.  .379-002  .223-001  .102+000  .128-002  .229+000
 300.  .329-002  .209-001  .108+000  .126-002  .220+000
 330.  .291-002  .199-001  .115+000  .126-002  .212+000
 360.  .258-002  .189-001  .121+000  .128-002  .205+000
 390.  .236-002  .192-001  .129+000  .135-002  .204+000
 420.  .218-002  .195-001  .137+000  .138-002  .203+000
 450.  .207-002  .202-001  .146+000  .145-002  .205+000
 480.  .198-002  .210-001  .154+000  .155-002  .208+000
 510.  .192-002  .216-001  .159+000  .170-002  .210+000
 540.  .186-002  .223-001  .163+000  .193-002  .213+000
 570.  .160-002  .230-001  .165+000  .214-002  .216+000
 600.  .130-002  .233-001  .167+000  .229-002  .218+000
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DEMERJIAN CHEMISTRY 100% CASE
           NO        NO2        O3         PAN        NMOC
   0.  .450-001  .150-001  .600-001  .000       .498+000
  30.  .109-001  .362-001  .397-001  .245-005  .415+000
  60.  .980-002  .360-001  .494-001  .161-003  .379+000
  90.  .919-002  .374-001  .579-001  .292-003  .366+000
 120.  .823-002  .372-001  .677-001  .388-003  .350+000
 150.  .577-002  .302-001  .792-001  .452-003  .299+000
 180.  .397-002  .235-001  .903-001  .559-003  .257+000
 210.  .316-002  .221-001  .105+000  .805-003  .248+000
 240.  .244-002  .200-001  .122+000  .108-002  .238+000
 270.  .172-002  .170-001  .140+000  .134-002  .223+000
 300.  .113-002  .137-001  .160+000  .161-002  .208+000
 330.  .719-003  .108-001  .181+000  .201-002  .194+000
 360.  .470-003  .844-002  .200+000  .232-002  .181+000
 390.  .342-003  .726-002  .222+000  .253-002  .173+000
 420.  .274-003  .657-002  .241+000  .253-002  .167+000
 450.  .237-003  .615-002  .259+000  .269-002  .162+000
 480.  .211-003  .588-002  .273+000  .293-002  .159+000
 510.  .199-003  .561-002  .282+000  .343-002  .157+000
 540.  .190-003  .546-002  .288+000  .415-002  .156+000
 570.  .168-003  .572-002  .292+000  .456-002  .157+000
 600.  .137-003  .576-002  .294+000  .456-002  .158+000
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```
CBIII CHEM SURF O3=.06 ALOFT O3=.04   ALL METHANOL VEHICLES
           NO        NO2        O3         PAN        NMOC
   0.  .450-001  .150-001  .600-001  .000       .501+000
  30.  .117-001  .351-001  .360-001  .130-003  .418+000
  60.  .124-001  .334-001  .367-001  .323-003  .383+000
  90.  .126-001  .341-001  .390-001  .569-003  .372+000
 120.  .121-001  .341-001  .429-001  .815-003  .358+000
 150.  .922-002  .285-001  .475-001  .948-003  .310+000
 180.  .661-002  .227-001  .531-001  .113-002  .266+000
 210.  .545-002  .220-001  .629-001  .159-002  .258+000
 240.  .443-002  .209-001  .737-001  .208-002  .250+000
 270.  .337-002  .189-001  .847-001  .251-002  .238+000
 300.  .248-002  .165-001  .967-001  .290-002  .225+000
 330.  .182-002  .144-001  .111+000  .341-002  .214+000
 360.  .133-002  .123-001  .124+000  .391-002  .203+000
 390.  .101-002  .110-001  .142+000  .455-002  .197+000
 420.  .801-003  .103-001  .158+000  .500-002  .193+000
 450.  .689-003  .100-001  .176+000  .547-002  .190+000
 480.  .620-003  .100-001  .191+000  .596-002  .189+000
 510.  .588-003  .101-001  .202+000  .653-002  .189+000
 540.  .569-003  .104-001  .209+000  .722-002  .190+000
 570.  .507-003  .111-001  .214+000  .773-002  .192+000
 600.  .429-003  .117-001  .218+000  .799-002  .194+000
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```
CBIII CHEM SURF O3=.03 ALOFT O3=.04    ALL METHANOL VEHICLES
           NO        NO2        O3        PAN         NMOC
   0.  .450-001  .150-001  .300-001  .000       .501+000
  30.  .174-001  .287-001  .197-001  .104-003  .415+000
  60.  .161-001  .289-001  .245-001  .276-003  .360+000
  90.  .154-001  .307-001  .288-001  .496-003  .368+000
 120.  .141-001  .317-001  .342-001  .715-003  .355+000
 150.  .101-001  .269-001  .411-001  .842-003  .305+000
 180.  .699-002  .219-001  .484-001  .103-002  .263+000
 210.  .574-002  .216-001  .585-001  .149-002  .256+000
 240.  .463-002  .207-001  .697-001  .197-002  .248+000
 270.  .351-002  .188-001  .809-001  .238-002  .236+000
 300.  .258-002  .165-001  .931-001  .277-002  .223+000
 330.  .189-002  .144-001  .107+000  .328-002  .213+000
 360.  .138-002  .124-001  .121+000  .378-002  .202+000
 390.  .104-002  .112-001  .138+000  .442-002  .196+000
 420.  .825-003  .104-001  .155+000  .488-002  .192+000
 450.  .706-003  .101-001  .173+000  .537-002  .190+000
 480.  .633-003  .101-001  .188+000  .587-002  .188+000
 510.  .598-003  .102-001  .199+000  .644-002  .188+000
 540.  .579-003  .104-001  .207+000  .713-002  .189+000
 570.  .516-003  .111-001  .211+000  .765-002  .192+000
 600.  .435-003  .118-001  .215+000  .790-002  .194+000
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```
cit chem surf o3=.06, aloft o3=.04
           NO        NO2        O3        PAN         NMOC
   0.  .450-001  .150-001  .600-001  .000       .500+000
  30.  .115-001  .348-001  .399-001  .148-003  .410+000
  60.  .117-001  .333-001  .429-001  .355-003  .371+000
  90.  .118-001  .343-001  .465-001  .567-003  .357+000
 120.  .114-001  .343-001  .507-001  .717-003  .342+000
 150.  .904-002  .283-001  .536-001  .737-003  .293+000
 180.  .680-002  .226-001  .574-001  .820-003  .252+000
 210.  .615-002  .226-001  .644-001  .983-003  .245+000
 240.  .556-002  .223-001  .712-001  .109-002  .238+000
 270.  .483-002  .213-001  .767-001  .110-002  .228+000
 300.  .417-002  .201-001  .821-001  .107-002  .218+000
 330.  .366-002  .193-001  .883-001  .107-002  .210+000
 360.  .323-002  .184-001  .938-001  .107-002  .204+000
 390.  .292-002  .188-001  .103+000  .113-002  .202+000
 420.  .267-002  .192-001  .111+000  .115-002  .201+000
 450.  .250-002  .200-001  .120+000  .122-002  .203+000
 480.  .237-002  .209-001  .128+000  .131-002  .205+000
 510.  .229-002  .217-001  .134+000  .145-002  .207+000
 540.  .222-002  .224-001  .138+000  .167-002  .210+000
 570.  .193-002  .234-001  .140+000  .186-002  .214+000
 600.  .158-002  .239-001  .142+000  .200-002  .216+000
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cit chem surf o3=.03, aloft o3=.04
          NO        NO2         O3         PAN        NMOC
   0. .450-001 .150-001 .300-001 .000       .500+000
  30. .183-001 .279-001 .202-001 .515-004 .409+000
  60. .163-001 .290-001 .269-001 .203-003 .371+000
  90. .153-001 .313-001 .328-001 .391-003 .357+000
 120. .140-001 .322-001 .389-001 .542-003 .341+000
 150. .105-001 .272-001 .446-001 .587-003 .292+000
 180. .775-002 .222-001 .498-001 .643-003 .251+000
 210. .690-002 .224-001 .570-001 .818-003 .244+000
 240. .618-002 .222-001 .640-001 .931-003 .237+000
 270. .532-002 .213-001 .700-001 .961-003 .227+000
 300. .456-002 .202-001 .758-001 .946-003 .217+000
 330. .398-002 .195-001 .822-001 .956-003 .210+000
 360. .350-002 .187-001 .879-001 .971-003 .203+000
 390. .315-002 .190-001 .962-001 .103-002 .202+000
 420. .287-002 .194-001 .104+000 .105-002 .201+000
 450. .269-002 .202-001 .113+000 .112-002 .202+000
 480. .255-002 .212-001 .121+000 .120-002 .205+000
 510. .246-002 .220-001 .127+000 .134-002 .207+000
 540. .239-002 .228-001 .130+000 .155-002 .210+000
 570. .208-002 .238-001 .133+000 .174-002 .214+000
 600. .170-002 .244-001 .135+000 .187-002 .216+000
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DEMERJIAN CHEM SURF O3=.06, ALOFT O3=.04
          NO        NO2         O3         PAN        NMOC
   0. .450-001 .150-001 .600-001 .000       .498+000
  30. .127-001 .345-001 .326-001 .196-005 .415+000
  60. .125-001 .336-001 .362-001 .124-003 .379+000
  90. .120-001 .350-001 .414-001 .209-003 .366+000
 120. .110-001 .352-001 .481-001 .268-003 .351+000
 150. .812-002 .289-001 .540-001 .297-003 .301+000
 180. .579-002 .231-001 .605-001 .347-003 .259+000
 210. .470-002 .225-001 .731-001 .487-003 .251+000
 240. .374-002 .213-001 .869-001 .647-003 .242+000
 270. .278-002 .191-001 .101+000 .777-003 .229+000
 300. .197-002 .164-001 .117+000 .918-003 .216+000
 330. .135-002 .139-001 .136+000 .118-002 .204+000
 360. .884-003 .112-001 .155+000 .152-002 .191+000
 390. .582-003 .945-002 .182+000 .192-002 .183+000
 420. .412-003 .811-002 .205+000 .215-002 .176+000
 450. .325-003 .730-002 .229+000 .244-002 .171+000
 480. .274-003 .680-002 .247+000 .274-002 .167+000
 510. .248-003 .638-002 .259+000 .326-002 .165+000
 540. .232-003 .615-002 .267+000 .399-002 .163+000
 570. .201-003 .635-002 .273+000 .441-002 .164+000
 600. .161-003 .636-002 .276+000 .442-002 .165+000
```

```
OZONE ALOFT O3=0.04 PPM, SURFACE O3=0.03 DEMERJIAN CHEMISTRY
          NO        NO2         O3        PAN        NMOC
   0. .450-001 .150-001 .300-001 .000          .498+000
  30. .199-001 .274-001 .166-001 .681-006 .415+000
  60. .171-001 .293-001 .230-001 .783-004 .380+000
  90. .154-001 .322-001 .297-001 .147-003 .367+000
 120. .134-001 .335-001 .376-001 .203-003 .352+000
 150. .940-002 .284-001 .459-001 .242-003 .301+000
 180. .648-002 .230-001 .541-001 .298-003 .260+000
 210. .522-002 .227-001 .667-001 .426-003 .252+000
 240. .415-002 .217-001 .803-001 .571-003 .243+000
 270. .308-002 .196-001 .942-001 .686-003 .230+000
 300. .220-002 .171-001 .110+000 .811-003 .217+000
 330. .153-002 .146-001 .128+000 .105-002 .206+000
 360. .102-002 .120-001 .147+000 .137-002 .194+000
 390. .666-003 .102-001 .174+000 .178-002 .186+000
 420. .460-003 .864-002 .199+000 .206-002 .178+000
 450. .353-003 .768-002 .223+000 .239-002 .173+000
 480. .291-003 .708-002 .243+000 .271-002 .170+000
 510. .261-003 .660-002 .256+000 .324-002 .167+000
 540. .242-003 .633-002 .264+000 .398-002 .166+000
 570. .208-003 .650-002 .270+000 .440-002 .166+000
 600. .167-003 .650-002 .274+000 .442-002 .167+000
```

```
CBM III CHEM  HCHO/MENO2=10%/5% WITH ALL METHANOL VEHICLES
          NO        NO2         O3        PAN        NMOC
   0. .450-001 .150-001 .600-001 .000          .501+000
  30. .101-001 .366-001 .434-001 .143-003 .417+000
  60. .982-002 .359-001 .500-001 .369-003 .383+000
  90. .965-002 .368-001 .551-001 .667-003 .370+000
 120. .907-002 .366-001 .614-001 .979-003 .357+000
 150. .651-002 .301-001 .711-001 .117-002 .306+000
 180. .454-002 .237-001 .807-001 .145-002 .263+000
 210. .381-002 .225-001 .915-001 .213-002 .256+000
 240. .311-002 .207-001 .104+000 .282-002 .247+000
 270. .234-002 .182-001 .116+000 .343-002 .234+000
 300. .170-002 .154-001 .130+000 .400-002 .220+000
 330. .124-002 .131-001 .145+000 .466-002 .209+000
 360. .927-003 .111-001 .158+000 .518-002 .198+000
 390. .739-003 .102-001 .175+000 .581-002 .192+000
 420. .631-003 .984-002 .191+000 .613-002 .187+000
 450. .575-003 .989-002 .207+000 .651-002 .184+000
 480. .538-003 .101-001 .221+000 .694-002 .183+000
 510. .520-003 .103-001 .231+000 .747-002 .182+000
 540. .509-003 .106-001 .238+000 .817-002 .183+000
 570. .456-003 .113-001 .243+000 .869-002 .185+000
 600. .386-003 .120-001 .246+000 .895-002 .187+000
```

```
cit chem hcho/meno2=10%/5% all ch4o vehicles
           NO          NO2         O3          PAN         NMOC
   0.  .450-001  .150-001  .600-001  .000       .500+000
  30.  .967-002  .356-001  .480-001  .163-003  .407+000
  60.  .911-002  .346-001  .573-001  .417-003  .367+000
  90.  .898-002  .357-001  .637-001  .684-003  .352+000
 120.  .862-002  .358-001  .702-001  .883-003  .337+000
 150.  .655-002  .296-001  .775-001  .907-003  .289+000
 180.  .493-002  .239-001  .839-001  .955-003  .250+000
 210.  .452-002  .235-001  .911-001  .119-002  .242+000
 240.  .415-002  .230-001  .982-001  .134-002  .235+000
 270.  .363-002  .219-001  .105+000  .139-002  .226+000
 300.  .314-002  .205-001  .111+000  .138-002  .216+000
 330.  .277-002  .196-001  .118+000  .140-002  .208+000
 360.  .245-002  .186-001  .124+000  .142-002  .201+000
 390.  .223-002  .187-001  .133+000  .151-002  .199+000
 420.  .205-002  .189-001  .142+000  .155-002  .198+000
 450.  .193-002  .196-001  .151+000  .165-002  .198+000
 480.  .184-002  .204-001  .160+000  .177-002  .200+000
 510.  .177-002  .209-001  .166+000  .196-002  .202+000
 540.  .171-002  .215-001  .170+000  .222-002  .205+000
 570.  .147-002  .222-001  .173+000  .247-002  .208+000
 600.  .119-002  .224-001  .175+000  .265-002  .209+000
```

```
DEMERJIAN CHEM HCHO/MENO2=10%/5% WITH ALL METHANOL VEHICLES
           NO          NO2         O3          PAN         NMOC
   0.  .450-001  .150-001  .600-001  .000       .498+000
  30.  .110-001  .363-001  .397-001  .247-005  .415+000
  60.  .978-002  .361-001  .496-001  .168-003  .379+000
  90.  .913-002  .375-001  .583-001  .306-003  .366+000
 120.  .815-002  .373-001  .684-001  .409-003  .350+000
 150.  .570-002  .303-001  .802-001  .478-003  .299+000
 180.  .377-002  .237-001  .915-001  .584-003  .256+000
 210.  .309-002  .221-001  .107+000  .862-003  .247+000
 240.  .237-002  .199-001  .125+000  .117-002  .236+000
 270.  .164-002  .168-001  .144+000  .146-002  .221+000
 300.  .107-002  .135-001  .164+000  .178-002  .205+000
 330.  .679-003  .107-001  .187+000  .222-002  .191+000
 360.  .454-003  .850-002  .206+000  .252-002  .177+000
 390.  .340-003  .748-002  .229+000  .272-002  .168+000
 420.  .283-003  .687-002  .248+000  .271-002  .161+000
 450.  .243-003  .646-002  .266+000  .286-002  .157+000
 480.  .216-003  .617-002  .281+000  .309-002  .153+000
 510.  .203-003  .586-002  .290+000  .359-002  .150+000
 540.  .193-003  .568-002  .296+000  .433-002  .149+000
 570.  .170-003  .591-002  .299+000  .475-002  .150+000
 600.  .137-003  .594-002  .302+000  .475-002  .151+000
```

```
CBM III CHEM  HCHO/MENO2=20%/1% WITH ALL METHANOL VEHICLES
          NO        NO2        O3        PAN       NMOC
   0. .450-001 .150-001 .600-001 .000      .501+000
  30. .942-002 .366-001 .462-001 .230-003 .415+000
  60. .879-002 .356-001 .549-001 .568-003 .379+000
  90. .834-002 .361-001 .621-001 .100-002 .364+000
 120. .760-002 .354-001 .703-001 .145-002 .349+000
 150. .543-002 .286-001 .802-001 .168-002 .298+000
 180. .377-002 .221-001 .895-001 .196-002 .256+000
 210. .310-002 .206-001 .102+000 .274-002 .247+000
 240. .247-002 .186-001 .115+000 .352-002 .238+000
 270. .183-002 .159-001 .128+000 .418-002 .224+000
 300. .132-002 .133-001 .141+000 .472-002 .211+000
 330. .976-003 .112-001 .155+000 .524-002 .199+000
 360. .751-003 .960-002 .166+000 .555-002 .189+000
 390. .622-003 .899-002 .181+000 .592-002 .184+000
 420. .549-003 .880-002 .195+000 .607-002 .179+000
 450. .511-003 .895-002 .210+000 .633-002 .177+000
 480. .485-003 .922-002 .223+000 .668-002 .176+000
 510. .474-003 .945-002 .232+000 .715-002 .176+000
 540. .467-003 .977-002 .239+000 .779-002 .177+000
 570. .422-003 .105-001 .243+000 .828-002 .179+000
 600. .358-003 .111-001 .246+000 .850-002 .181+000
```

```
cit chem hcho/meno2=20%/1% all ch4o vehicles
          NO        NO2        O3        PAN        NMOC
   0. .450-001 .150-001 .600-001 .000       .500+000
  30. .897-002 .361-001 .522-001 .263-003 .404+000
  60. .810-002 .349-001 .642-001 .645-003 .361+000
  90. .775-002 .356-001 .729-001 .103-002 .345+000
 120. .728-002 .352-001 .810-001 .130-002 .328+000
 150. .557-002 .287-001 .876-001 .128-002 .280+000
 180. .423-002 .228-001 .929-001 .127-002 .241+000
 210. .386-002 .223-001 .101+000 .152-002 .234+000
 240. .352-002 .217-001 .108+000 .167-002 .226+000
 270. .307-002 .204-001 .115+000 .170-002 .217+000
 300. .265-002 .190-001 .121+000 .166-002 .207+000
 330. .234-002 .181-001 .128+000 .165-002 .200+000
 360. .207-002 .171-001 .134+000 .165-002 .193+000
 390. .188-002 .172-001 .144+000 .173-002 .191+000
 420. .173-002 .174-001 .153+000 .177-002 .189+000
 450. .163-002 .180-001 .163+000 .185-002 .190+000
 480. .155-002 .186-001 .172+000 .197-002 .191+000
 510. .149-002 .191-001 .179+000 .215-002 .193+000
 540. .144-002 .195-001 .183+000 .242-002 .195+000
 570. .124-002 .201-001 .186+000 .266-002 .198+000
 600. .994-003 .202-001 .188+000 .284-002 .200+000
```

```
DEMERJIAN CHEM HCHO/MENO2=20%/1% WITH ALL METHANOL VEHICLES
            NO        NO2        O3        PAN        NMOC
   0. .450-001 .150-001 .600-001 .000       .498+000
  30. .109-001 .362-001 .397-001 .238-005 .414+000
  60. .899-002 .360-001 .533-001 .244-003 .374+000
  90. .792-002 .370-001 .656-001 .458-003 .357+000
 120. .680-002 .363-001 .789-001 .616-003 .340+000
 150. .471-002 .289-001 .914-001 .687-003 .289+000
 180. .318-002 .221-001 .103+000 .802-003 .248+000
 210. .245-002 .202-001 .121+000 .114-002 .237+000
 240. .182-002 .177-001 .140+000 .152-002 .225+000
 270. .122-002 .144-001 .160+000 .187-002 .209+000
 300. .772-003 .113-001 .180+000 .217-002 .194+000
 330. .505-003 .887-002 .200+000 .248-002 .180+000
 360. .370-003 .722-002 .215+000 .259-002 .168+000
 390. .284-003 .649-002 .235+000 .267-002 .161+000
 420. .241-003 .605-002 .250+000 .260-002 .155+000
 450. .214-003 .576-002 .266+000 .273-002 .151+000
 480. .194-003 .557-002 .280+000 .295-002 .148+000
 510. .186-003 .535-002 .287+000 .343-002 .146+000
 540. .179-003 .524-002 .293+000 .415-002 .145+000
 570. .160-003 .552-002 .296+000 .455-002 .145+000
 600. .131-003 .559-002 .298+000 .455-002 .146+000
```

```
CBM III CHEM  HCHO/MENO2=20%/5% WITH ALL METHANOL VEHICLES
            NO        NO2        O3        PAN        NMOC
   0. .450-001 .150-001 .600-001 .000       .501+000
  30. .937-002 .366-001 .464-001 .238-003 .415+000
  60. .873-002 .356-001 .552-001 .589-003 .378+000
  90. .829-002 .362-001 .626-001 .103-002 .363+000
 120. .760-002 .357-001 .709-001 .147-002 .348+000
 150. .543-002 .288-001 .807-001 .168-002 .297+000
 180. .378-002 .223-001 .900-001 .198-002 .255+000
 210. .309-002 .208-001 .102+000 .279-002 .246+000
 240. .246-002 .187-001 .116+000 .362-002 .237+000
 270. .182-002 .161-001 .129+000 .433-002 .223+000
 300. .131-002 .134-001 .143+000 .492-002 .209+000
 330. .971-003 .114-001 .157+000 .549-002 .197+000
 360. .755-003 .984-002 .169+000 .583-002 .187+000
 390. .633-003 .936-002 .186+000 .628-002 .181+000
 420. .564-003 .925-002 .200+000 .643-002 .176+000
 450. .527-003 .947-002 .216+000 .671-002 .174+000
 480. .502-003 .978-002 .229+000 .708-002 .172+000
 510. .489-003 .100-001 .239+000 .757-002 .171+000
 540. .481-003 .103-001 .246+000 .824-002 .172+000
 570. .432-003 .111-001 .250+000 .875-002 .174+000
 600. .366-003 .117-001 .253+000 .901-002 .176+000
```

```
cit chem hcho/meno2=20%/5% all ch4o vehicles
            NO         NO2         O3         PAN         NMOC
    0.  .450-001  .150-001  .600-001  .000        .500+000
   30.  .866-002  .356-001  .528-001  .271-003  .401+000
   60.  .781-002  .342-001  .653-001  .674-003  .358+000
   90.  .750-002  .351-001  .741-001  .108-002  .341+000
  120.  .706-002  .347-001  .824-001  .136-002  .324+000
  150.  .544-002  .284-001  .889-001  .135-002  .278+000
  180.  .413-002  .226-001  .942-001  .135-002  .240+000
  210.  .375-002  .221-001  .102+000  .161-002  .232+000
  240.  .342-002  .215-001  .110+000  .179-002  .224+000
  270.  .297-002  .202-001  .117+000  .183-002  .214+000
  300.  .256-002  .189-001  .124+000  .180-002  .204+000
  330.  .225-002  .179-001  .131+000  .180-002  .196+000
  360.  .198-002  .169-001  .138+000  .181-002  .189+000
  390.  .179-002  .170-001  .148+000  .192-002  .187+000
  420.  .164-002  .171-001  .158+000  .197-002  .184+000
  450.  .154-002  .177-001  .169+000  .209-002  .184+000
  480.  .146-002  .183-001  .179+000  .223-002  .185+000
  510.  .140-002  .187-001  .186+000  .244-002  .186+000
  540.  .135-002  .191-001  .191+000  .275-002  .188+000
  570.  .115-002  .196-001  .194+000  .303-002  .190+000
  600.  .917-003  .196-001  .196+000  .324-002  .192+000
```

```
DEMERJIAN CHEM HCHO/MENO2=20%/5% ALL METHANOL VEHICLES
            NO         NO2         O3         PAN         NMOC
    0.  .450-001  .150-001  .600-001  .000        .498+000
   30.  .110-001  .363-001  .397-001  .240-005  .414+000
   60.  .897-002  .361-001  .535-001  .252-003  .374+000
   90.  .788-002  .371-001  .661-001  .476-003  .357+000
  120.  .674-002  .364-001  .797-001  .644-003  .339+000
  150.  .465-002  .290-001  .925-001  .721-003  .288+000
  180.  .313-002  .221-001  .104+000  .849-003  .247+000
  210.  .240-002  .201-001  .123+000  .122-002  .235+000
  240.  .176-002  .176-001  .143+000  .165-002  .223+000
  270.  .117-002  .144-001  .164+000  .204-002  .207+000
  300.  .738-003  .112-001  .185+000  .237-002  .191+000
  330.  .492-003  .896-002  .205+000  .268-002  .176+000
  360.  .362-003  .746-002  .221+000  .277-002  .164+000
  390.  .291-003  .681-002  .241+000  .283-002  .156+000
  420.  .248-003  .638-002  .257+000  .275-002  .150+000
  450.  .221-003  .606-002  .273+000  .287-002  .145+000
  480.  .199-003  .583-002  .287+000  .309-002  .142+000
  510.  .189-003  .558-002  .295+000  .358-002  .139+000
  540.  .182-003  .543-002  .300+000  .431-002  .138+000
  570.  .162-003  .570-002  .303+000  .472-002  .138+000
  600.  .132-003  .575-002  .305+000  .472-002  .139+000
```

APPENDIX E

DISCUSSION OF THE CIT 50 PERCENT METHANOL SCENARIO SUBSTITUTION

APPENDIX E

The modeling results of the CIT 50% methanol conversion scenario are highly unusual. The objective of this section is to discuss potential causes for the suspect results of this modeling scenario with the CIT mechanism.

There are four major potential causes for the results of the CIT 50% conversion scenario. These causes are

1) improper input data,
2) improper functioning of the model,
3) improper functioning of the mechanism due to improper installation in the model, and
4) inability of the mechanism to accurately simulate the specific case modeled.

Improper Input Data

It is highly unlikely that improper input data are the cause for the poor results on the 50% conversion scenario. Tables E-1 and E-2 present the input data, as transcribed from the run printouts, for the CIT base case, 50%, and 100% conversion scenarios. The data in Table E-1 are the initial parcel concentrations, in ppmV, for each of the three runs. The data in Table E-2 are the remaining data input into the model for each run. All the data in Table E-2 were identical for each run including NO_2 photolysis rates, meteorological parameters, and emission fractions. Consequently, the only input differences between the runs are those contained in Table E-1.

The last two columns in Table E-1 present the difference in concentration for each species between the 50% case and base case and between the

TABLE E-1. MODELED PARCEL INITIAL CONCENTRATIONS (ppmV)

	Scenario			Concentration Differences	
Species	Base Case	50% Methanol Conversion	100% Methanol Conversion	50% Less Base Case	100% Less 50% Case
NO_2	0.0150	0.0150	0.0150	0.0	0.0
NO	0.0450	0.0450	0.045	0.0	0.0
O_3	0.0600	0.0600	0.0600	0.0	0.0
ALK	0.0620	0.0508	0.0384	−0.0112	−0.0124
ETH	0.0133	0.0098	0.0065	−0.0035	−0.0033
OLE	0.0190	0.0121	0.0062	−0.0069	−0.0059
ARO	0.0104	0.0076	0.0050	−0.0028	−0.0026
HCHO	0.0055	0.0162	0.0269	0.0107	0.0107
RCHO	0.0038	0.0032	0.0025	−0.0006	−0.0007
CH_3OH	0.0	0.1025	0.2050	0.1025	0.1025
$MeNO_2$	0.0	0.0011	0.0023	0.0011	0.0012
CO	0.0	0.0011	0.0023	0.0011	0.0012
H_2O_2	1.0E−6	1.0E−6	1.0E−6	0.0	0.0

TABLE E-2. HOURLY INPUT PARAMETERS FOR THE CIT MECHANISM SENSITIVITY RUNS[a]

Time Since 8:00 (min)	NO_2 Photoylsis Rate (min^{-1})	Temperature (°C)	Mixing Height (m)	Emission Fractions		
				NO	NO_2	NMOC[b]
0	0.2678	23	70	0.24	0.72	0.23
60	0.3792	26	116	0.24	0.72	0.23
120	0.4405	29	156	0.24	0.72	0.23
180	0.4797	32	300	0.24	0.72	0.23
240	0.5009	33	356	0.24	0.72	0.23
300	0.5077	36	447	0.24	0.72	0.23
360	0.4992	37	528	0.24	0.72	0.23
420	0.4761	38	539	0.24	0.72	0.23
480	0.4323	36	523	0.24	0.72	0.23
540	0.3610	29	520	0.24	0.72	0.23
600	0.2496	29	520	0.24	0.72	0.23

[a] The same input data, except initial parcel concentrations, were used for all the CIT mechanism sensitivity runs.

[b] An hourly emission fraction of 0.23 was used for each species emitted. These species were: ALK, ETH, OLE, ARO, RCHO, HCH, CH_3OH, $MeNO_3$.

50% and 100% cases. There should be equal, linear changes in initial concentration going from the base case to the 50% case and then to the 100% case. As can be seen in Table E-1, the differences are equal except for rounding errors. There is no discontinuity in the progression of initial conditions that could explain the unusual results of the 50% conversion scenario.

Improper Functioning of the GCKM Model

It is possible that the GCKM model used to perform the modeling has an error in the coding that results in the unusual results of the 50% conversion modeling scenario. The GCKM model was used for modeling all the other scenarios and for other modeling projects performed at Radian without similar unusual results occurring. Thus, while possible, the probability of a model "bug" is probably lower than that of an improper incorporation of the CIT mechanism in the model. Without further analysis, however, a model "bug" cannot be ruled out.

Improper Installation of the Mechanism

The most likely reason for the unusual results is improper installation of the CIT mechanism in the GCKM model. As discussed in 4.0, Radian was unable to obtain a test case from the developers of the CIT mechanism. Without such a test case, it was not possible to ensure proper functioning of the mechanism.

Inability of CIT Mechanism to Simulate the Scenario

It is possible, but unlikely, that the CIT mechanism has a "bug" in it that manifests itself during the 50% conversion scenario. Again, without further analysis and a test case from the developers, the proper functioning of the CIT mechanism cannot be ensured.